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TALANTA REVIEW*

A CRITICAL REVIEW OF NEUTRON ACTIVATION AND TRACER METHODS FOR THE DETERMINATION OF THE NOBLE METALS

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Summary—Neutron activation methods for the seven noble metals are critically reviewed up to December, 1965. The methods deal with the determination of trace impurities in each noble metal as well as traces of noble metals in media such as organic material, fission product and other solutions, ores, alloys, minerals, silica and base metals. The need for confirmatory evidence in the case of such complex materials as ores is emphasized.

THIS review deals with the analysis of the noble metals by methods which involve measurements of radioactivity and have been recorded in *Chemical Abstracts* and in miscellaneous sources of activation procedures up to and including December, 1965. An effort has been made to restrict detailed discussion to methods which provide general approaches to the determination of trace impurities in noble metals, or deal with traces of noble metals in various materials, or include typical methods of chemical separation.

Activation techniques are principally applied to determination of submicrogram amounts of constituents and so would not be expected to replace to an appreciable extent such established techniques of trace analysis as optical or X-ray spectrography, *etc.* However, for determination of submicrogram traces, no analytical tool of comparable value is available to the analytical chemist, and one may confidently expect rapid developments in neutron activation techniques.

These developments will include simpler and better methods of protection, more readily available sources of activation energy, cheaper measuring instruments, improved techniques of chemical separation, direct methods needing no prior chemical treatment, and a growing supply of trained technical operators. Smales[1] has stated that neutron activation methods "will grow steadily as analytical chemists become aware of its advantages and as training in elementary radiochemistry becomes more widespread. The techniques are quite easily learned, the cost of equipment is not outrageous by modern analytical standards, the cost of irradiation per sample is quite small, very few special laboratory modifications are required, and any health

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hazard can be kept well under control at the levels required for most applications." The significant observation is also made that "like any other method of analysis, radioactivation has its limitations, and the user should be aware of them. There has undoubtedly been a tendency in published papers (neutron activation methods) so far to stress the advantages and neglect the limitations." Smales[1] dealt with problems associated with the decomposition of samples and containers under irradiation conditions. That unexpected decomposition difficulties can occur was made evident in an experiment by the present authors in which a violent decomposition of an activated solution of iridium occured after removal of the silica tubes from the aluminium radiation capsule. Although the cause of this explosion was not determined, it may have been the catalytic effect of iridium.

Accurate manipulations and analytical experience are just as necessary in activation techniques as in classical analysis, and chemical recovery determinations are not necessarily an adequate substitute. Published procedures do not always indicate the errors which can be associated with the chemical recovery method which may itself be partly invalidated by inapplicable variations in technique. Examples are discussed below for ores and concentrates, *etc.* Indeed, some proposed methods can only be used for liquid extracts from the ores. It may be emphasized that procedures applicable to the accurate determination of milligram amounts of noble metals of submicrogram quantities are not necessarily suitable for the chemical recovery by acid extractions.

There is also the problem of securing representative samples, especially in the case of ores, *etc.*, and particularly in the case of gold, which may occur in grains or nuggets. With these materials the use of the assay ton in the classical methods assists in achieving accuracy and precision of recovery. The problem of securing a representative sample of the size required for neutron activation increases the difficulty of obtaining results comparable to those obtained with the classical assay. No satisfactory comparison of results obtained by activation methods and by other established methods has so far appeared, and until one does, the activation methods must in general remain suspect when applied to such problems. Despite the different orders of magnitude of sensitivity, concentration methods can be applied to allow reasonable comparisons to be made when the concentrations of noble metal can be made appropriate to both classical and activation methods. Perhaps the greatest difficulty in making such comparisons lies not in the deficient sensitivities of the more established trace methods, but in ensuring the purity of the reagents used to concentrate the traces. For the determination of microgram and submicrogram traces of noble metals in rocks and ores no analytical procedure or technique yet recorded can be accepted as invariably accurate.

The few recorded results comparing the accuracy of the activation and established methods were not obtained under the conditions necessary to establish relative accuracy. For example, the spectrographic determinations of iridium in the metal phase of chondritic meteorites made by Nichiporuk and Brown[2] gave values that agreed closely with those obtained by Rushbrook, Ehmann *et al.*[3] by neutron activation procedures for other chondrites of known metal content, but both values can only be accepted with the reservation that such spectrographic results also require some confirmation.

It would seem that none of the neutron activation methods proposed for the

determination of the noble metals should be considered invariably applicable to samples of ores containing some of the most resistant types of noble metal minerals. A more extensive knowledge of naturally occurring, mechanically mixed, and dissolved noble metal constituents is needed. Without this knowledge, one cannot with complete assurance provide the standards which must be the basis for achieving accuracy within the theoretical limits of the techniques used.

Fukai and Meinke[4] gave an interesting discussion of the relative sensitivities of neutron activation and specific spectrophotometric methods. Sensitivity for neutron activation methods was defined as "the weight of an element that would produce a measurable amount of radioactivity after it had been irradiated by a given flux of neutrons for a given period of time." The general equation expressing the significant relationships was given as:

$$\frac{\text{activity} \times \text{atomic weight}}{6{\cdot}02 \times 10^{23} \times f \times \theta \times \sigma_{at}\left[1 - \exp\left(\frac{0{\cdot}693t}{t_{1/2}}\right)\right]}.$$

Neglecting the constants, the weight detectable is a function of activity, the cross section (σ_{at}), the flux (f), the half-life ($t_{\frac{1}{2}}$) and the time of irradiation (t). Sensitivity may be improved by a proper selection of these variables and use of suitably sensitive detecting instruments. Tables of sensitivity limits for various isotopes have been recorded, using arbitrarily chosen variables. Fukai and Meinke modified Schindewolf's[5] choice of variables by including a flux of 5×10^{11} neutrons.cm^{-2}.sec^{-1} and compared the sensitivities for noble metals with spectrophotometric data based on Sandell's sensitivity index[6] and a 5-ml volume used for the absorbance measurements. The sensitivities were expressed in weights and not in concentrations. The authors included comparisons on the basis of a sensitivity index defined as the negative logarithm of the sensitivity expressed in weight. The following results were recorded (the index for neutron activation is given in brackets): for osmium determined by thiourea 4·7 (7·4); for ruthenium by thiourea 6·0 (7·6); for rhodium by tin(II) chloride 5·7 (7·6); for iridium as chloroiridate 4·7 (9·7); for palladium by nitrosodiphenylamine, 6·3 (8·6); for platinum by tin(II) chloride 4·7 (7·7); for gold by rhodamine 6·7 (9·2). Although these figures are subject to variations depending on the choice of techniques or significant variables, the neutron activation methods seem to be more sensitive by 1 or 2 orders of magnitude. The activation sensitivities may be increased by irradiation for longer periods and by the use of higher neutron fluxes.

Jenkins and Smales[7] gave a table of estimated sensitivities for noble metals and other elements, based on an assumed irradiation with a flux of 10^{12} neutrons.cm^{-2}.sec^{-1} for 1 month followed by a 2-hr decay during which radiochemical purification is made with a quantitative yield. In the case of the noble metals, for which no procedures giving a quantitative yield have been recorded, the sensitivities provide only a guide for comparison with other trace methods. For 2·7 d gold-198 the estimated sensitivity 5×10^{-12} g; for 4·5 hr ruthenium-105, 1×10^{-9}; for 31 hr osmium-193, 1×10^{-9}; for 4·3 min rhodium-104m/rhodium-104, 5×10^{-3}; for 19 hr iridium-194, 1×10^{-11} for 18 hr platinum-197 with platinum-199, 1×10^{-9}. It must be emphasized that these sensitivities are theoretically derived and are seldom realized in the determination of noble metals because of interference from associated traces and radioactive phenomena. Jenkins and Smales state that the coefficient of variation normally

obtained at these sensitivities should be $<10\%$ for single determinations, and at higher concentrations might be only 1%. As with other methods the precision increases with an increase in the proportion of the trace element, and is affected by the background, which may be a composite effect of contaminants and the intrinsic background of the counting assembly.

Jenkins and Smales state that the method will provide high accuracy "if the activated species passes completely into true solution, without loss by volatility, adsorption, or persistent traces of insoluble residues, and if the dissolved species undergoes complete isotopic exchange with the added carrier." The present authors emphasize that the carrier element must be in the same form as the element to be determined. To achieve this, particularly in the case of ores, the sample and carrier should be thoroughly mixed, and fused or otherwise dissolved completely. Jenkins and Smales stated further that providing acceptable precision is secured, the absolute accuracy of the method depends on the availability of a standard whose composition is known to an accuracy greater than the maximum accuracy of the trace determination and the behaviour of the standard in activation must be exactly the same as that of the trace element to be determined. Though the activation method is less sensitive than spectrophotometric or even spectrographic methods to variations in solution composition or the identities of mechanically mixed constituents, those factors cannot be ignored, particularly in the case of trace determination of noble metals in rocks, ores, alloys etc. Unless adequate precautions have been taken, it should not always be assumed that the effective neutron flux is uniform for both sample and standard. Aside from variations in flux associated with the excitation source, variation in excitation resulting from self-shielding by the constituent being determined or absorption by other constituents must be considered. The essential difficulty here is common to all methods of determining trace constituents in materials such as rocks and is at least partially the result of a lack of knowledge of the identity of the noble metal mineral. However, if a homogeneous distribution of the noble metal constituent can be achieved, and particularly if the analytical chemist has adequate knowledge of the types of minerals probably present, selecting and preparing an activation standard is not difficult.

Each of the conditions for accuracy (mentioned by Jenkins and Smales), may be critical in the determination of traces of noble metals in naturally occurring materials. The problem of loss of platinum metals through volatility is of constant concern in their analysis but strangely has received little attention in the activation methods. Determining the chemical yield does not necessarily compensate for such losses. Obviously, in the preparation of samples for activation, losses resulting from oxide volatilization during heating and dissolution must be minimized particularly in the case of dissolution of osmium and ruthenium. If the noble metal constituent dissolved is not the same in the sample and the standards, an error that is not compensated by the standards can arise from volatilization after activation but before chemical separation.

Sufficient care is not always taken to achieve isotopic homogeneity in the solutions of the samples. Difficulty in achieving homogeneous isotopic distribution can be expected if the identity of the noble metal species extracted from the sample during the dissolution of sample and carrier is not fully known. Errors of this type could be minimized if carriers could be provided that were identical with the noble

metal constituent in the sample. That this inhomogeneity may be a critical factor has been shown for ruthenium*[8] and for fission product solutions[9].

Errors may also arise from incomplete dissolution of rock or alloy samples; residues often remain after acid treatments of ore samples and consist of a silicate or mixed silicates. Many activation methods for the determination of noble metal traces fail to direct attention to these residues, and usually there is the inference that the residue is to be discarded. Because of the ease with which noble metals react with silica to form corrosion-resisting compounds and/or solid solutions it is particularly important that all final residues be incorporated in the solution of the sample or at least be examined for noble metal traces. In the case of rocks, ores, *etc.*, in which such elements as iridium, rhodium, ruthenium and osmium, and silica are present together, particularly if the sample has been subjected to high temperatures, the residue should not be indiscriminately discarded.

A well-trained analytical chemist must find disconcerting the easy acceptance of such processes as hydrolytic precipitation, reduction, *etc.*, which invariably introduce some degree of difficulty into analytical methods and may not be devoid of error despite the device of chemical yield determination. It is not uncommon to find radiochemical methods involving a final precipitation of a noble metal by reduction with zinc or magnesium, or by hydrolytic methods. Such techniques tend to cause accumulation of contamination which is not always detected by the usual methods of determining radioactive purity, and may seriously affect the chemical yield. The analytical techniques normally used to ensure chemical purity are well known and their application is of particular importance in activation methods which give considerably less than quantitative yield.

The following review is arranged to deal collectively with procedures designed for specific materials such as fission product solutions, ores, rocks, silica, minerals, alloys and organic substances. In the case of those materials in which more than one noble metal is determined the discussions are collected under multi-component noble metal systems and again the discussions are arranged to deal with specific materials.

ACTIVATION METHODS APPLIED TO DETERMINE THE EFFICIENCY OF CHEMICAL SEPARATIONS

Neutron activation techniques are particularly useful for examination of the efficiency of analytical treatments of noble metals and for determining the losses and distribution of the noble metals in the various stages of industrial methods for their recovery and purification. Similarly, the techniques, properly arranged and applied, can provide useful information about the distribution of noble metals in the classical assay methods, *e.g.*, Kim *et al.*[10] have discussed the distribution of gold in the classical assay process. The gold content of each of the flux constituents, slags, pot wall, lead buttons and cupels was first determined qualitatively, significant amounts of gold being found only in the ore sample and the lead button. Negligible amounts of gold were found in the cupel area immediately adjacent to the gold bead. The quantitative results for the gold content of the ore sample and the assay button showed that recovery was acceptably complete and that there were negligible losses of gold at the various stages of a fire assay.

It is difficult to find an explanation for the authors' results. The gold values obtained by neutron activation for the lead buttons produced by the fire assay and for the ore sample were in close agreement, which suggests an effective recovery by fire assay. Calculations from the results show for the ore a value of 0·90 troy oz per ton and for the average of the lead buttons 0·89 oz per ton. However, the single value recorded from the fire assay procedure is 0·84 oz per ton. The significance of the

* It should be noted that the ruthenium isotope used was probably ^{106}Ru; ^{110} Ruis not now recognized.

discrepancy is emphasized by the good precision obtained by the activation method for ore and lead samples weighing only 200–600 mg. Obviously there is an appreciable error in either the fire assay results or in the activation results. This problem of effectively comparing the efficiency of the two methods has not yet been solved and without doubt will involve an extensive research programme. In any case, the authors' purpose was not primarily a comparison of the methods but rather to assess the distribution losses, which would not be significantly affected by the discrepancies.

Presumably, the authors failed to recognize that the fire assay loss of gold to slags, cupels, *etc.* may well prove to be a function of such variables as temperature, rate of air flow, type of cupel, *etc.* and that one cannot generalize about losses from specific procedures and assay materials. It should be noted that the fire assay for gold almost invariably involves a cupellation to produce a silver-gold bead and distribution data obtained for formation of a final gold bead need not correspond to those for a silver-gold bead. Nevertheless, the results obtained by Kim *et al.*[10] do show a promising approach to the problem of determining noble metal losses during fire assay procedures.

Kim *et al.* activated 0·2–0·6 g of the various types of samples at $1{\cdot}3 \times 10^{12}$ neutrons.cm^{-2}.sec^{-1} through the pneumatic transfer system and $0{\cdot}7 \times 10^{13}$ neutrons.cm^{-2}.sec^{-1} in a rotary specimen rack. The flux was monitored with gold foils taped to the inner side of the cap of the nylon rabbit. The irradiated samples were fused with sodium peroxide in the presence of carrier gold. The chemical procedure involved extractions with ethyl acetate, back-extraction with ammonia solution and precipitation with hydroquinone; the purity of the gold from samples and standards was checked by half-life measurements.

Losses of gold during the various stages of fire assay were also discussed by Shima[11]. Gold-198 was used as a tracer and activity measurements were made on *aqua regia* extracts from the pot wall, slags, cupels and cupelled beads. To determine the location of the losses to the pot wall and the bone ash cupel Shima used autoradiography with X-ray films. After the assay the pot and cupel were cut into two parts and a thin vinyl membrane was placed between the film and the sample half. A 3-day exposure was used.

It was shown that for the cupel the gold loss was concentrated in the bone ash adjacent to the cupelled bead surface. As stated above, Kim *et al.*[10] found this loss to be negligible. The losses to the pot wall were associated with that part of it in contact with the flux and above the area adajcent to the fused lead button. These findings would, of course, be predicted from the nature of the assay, *e.g.*, one would not expect the complete removal of gold from the wall of a beaker by simply draining an aqueous gold solution. A second cleaning fusion is always required for fire assays if good accuracy is to be obtained. In the case of the cupel loss it is also to be expected that traces of gold will accompany the adsorbed litharge as indicated by Shima's results and it may be hoped that this phase of a fire assay for noble metals will be subjected to a careful examination. Although a variety of phenomena may be associated with the adsorption of gold by the pot wall in contact with fused media, the authors have found no report which deals adequately with this technique despite the commercial significance of the method and the many decades of its application. It is an involved problem and will require a consideration of each of many factors which determine the efficiency of a cupellation.

Shima used ores with high sulphide, high copper and iron, with copper, lead, zinc and silver, and with high silicate contents. For each type the usual fluxes were applied, each containing 30 g of litharge, 2 g of flour and a cover of 12 g of sodium chloride. The iron nail method was used for high-sulphide charges.

No details were given for such essential conditions as methods of sampling and of mixing the tracer and sample, or for temperatures and rates of heating during fusion and cupellation. Shima concluded that of the ores examined, the highest gold losses to the pot wall occurred with samples containing high iron and sulphur with some copper. For the slags, the highest losses occurred with copper ores containing a high sulphur content. With the cupel, presumably the high losses of gold were associated with samples of a high base metal and sulphur content. The author stated that with the iron nail method the results were not conclusive. In general, it was concluded that the losses of gold will vary with the composition of the sample and that cupel losses are higher than losses to the pot wall.

In the present authors' opinion, while the conclusions may well prove to be valid, the techniques and the data described by the author allow only superficial conclusions to be reached, and the failure to recover the added gold quantitatively may be the result of inadequate technique rather than losses by evaporation on fusion and cupellation as suggested by the author.

Extensive researches on fire-assay, solvent extraction and ion-exchange separations of the noble metals were recorded by Beyermann.[12] Radioactive isotopes were used to follow the distribution of the noble metals during the separation processes. This report includes a wide variety of approaches to methods of separation and will be reviewed in a report concerned with methods of separating the noble metals.

The efficiency of various methods for the analytical separation of platinum metals was examined by Lloyd and Morris,[13] by neutron activation techniques. The hydrolytic separation of platinum and the subsequent separation of rhodium from iridium by titanium(III) chloride as described by Gilchrist[14] was compared with the chromotographic method used by Payne.[15]

In reports such as these, it must be assumed that the separations accomplished by the authors are optimum in efficiency for the particular method. Perhaps a greater degree of confidence in such reported results would result from an inclusion of all the quantitative results obtained from the procedures under investigation. Lloyd and Morris[13] used ^{192}Ir as ammonium hexachloroiridate as the tracer and measured the gamma activity. The results given for efficiency of separation are inconclusive and although the measured activity of the iridium recovered suggests quantitative recovery this interpretation would be invalidated if appreciable contamination by rhodium was present. The authors' principal conclusion, for which no evidence is given, seems to be that Payne's method is more rapid than Gilchrist's.

In contrast to this report, in a second paper Lloyd and Morris[16] provided adequate results to establish that platinum could be effectively determined gravimetrically in the presence of iridium, and also gave results for the separation and gravimetric determination of rhodium and iridium.

To precipitate platinum in 10-mg amounts the authors used three methods, in which the precipitants were a solution of mercury(II) chloride and hypophosphorous acid, or solid mercury(I) chloride, or a slurry of mercury(I) chloride. Each method was checked gravimetrically and by the use of iridium-192 tracer, with a final radiometric examination with a gamma-scintillation counter for traces of iridium in the precipitated platinum.

To precipitate rhodium, mercury(I) chloride slurry was added to the solution of rhodium and iridium chlorides, containing potassium bromide. The rhodium precipitate was dissolved by hot hydrochloric acid saturated with bromine. The gravimetric recoveries of rhodium from samples containing 10 mg each of rhodium and iridium were reasonably accurate and the iridium contamination of the rhodium amounted to about 6 μg as determined by counting iridium-192. For the determination of iridium in the filtrate, potassium iodide was added and the mixture was then boiled to produce a precipitate which was then heated to 900°, reduced in hydrogen, and weighed.

Traces of palladium, gold and iridium in residues from the recovery of platinum metals have been determined by neutron activation. Herak and Morris[17] determined microgram and submicrogram quantities of the three elements in 0·5 ml of solution. The procedure involved irradiation of the sample and standards and separation of the activities in the sample. For gold the gamma radiation from gold-198 was used; for palladium the beta radiation from palladium-109 or alternatively the X-rays associated with the equilibrium mixture of silver-109m and palladium-109 could be used; for iridium the gamma rays from iridium-192 were applied. The metals were determined in order of increasing half-life, *e.g.*, palladium 13·6 hr, gold 2·70 d, and iridium 74·4 d. Standards and samples were irradiated for 6 days with a flux of $1{\cdot}2 \times 10^{13}$ neutrons.cm^{-2}.sec^{-1}. The samples were dissolved and milligram amounts of metal standards were added as carriers. Gold was isolated by solvent extraction with isopropyl ether which was first washed with hydrochloric acid and then treated repeatedly with iridium carrier. The final ether extract was evaporated and the gold was precipitated by sulphur dioxide and weighed to determine the chemical yield. The gold from the standards and sample was determined by measuring the intensity of the 0·411 MeV gamma rays Corrections were made for background, chemical yield and for any decay between the times of counting of the precipitates from samples and standards.

For palladium the aqueous phase of the gold-ether extraction was subjected to hydrolysis in the presence of nitrite, to remove the base metals selectively. The palladium and iridium complexes in solution were decomposed with hydrochloric acid, and palladium dimethylglyoximate was separated. This was dissolved and the metal precipitated by hypophosphorous acid. Dissolution of the metal by nitric acid was followed by a silver chloride scavenge and finally palladium dimethylglyoximate was again isolated, and weighed to determine the chemical yield. All counting rates for the glyoximate were corrected for paralysis time, yield, *etc.*, as in the case of gold.

For the isolation of iridium the filtrate resulting from the removal of palladium from the decomposed nitrite complexes was treated to form hydrated iridium dioxide. This was dissolved and iridium was removed by the addition of mercury(I) chloride in the presence of bromide and iodide.[18] The oxide was converted into metal and weighed to determine the chemical yield, then the activity was counted by gamma spectrometry as described previously.[18] In each case, the use of similar weights of samples and standard avoided the need for self-absorption corrections. Presumably there was no interference from any of the nuclides used for measurements. Although the authors did not state the chemical yield their results indicate reasonable precision. It may be noted that contamination of the filtrate from the nitrite separation of base metal could result in erroneous chemical yields of iridium.

METHODS FOR INDIVIDUAL ELEMENTS

Gold

Fission products

To separate gold from associated fission-products Cowan[19] removed oxidizing substances and used sulphosalicylic acid to complex extraneous fission product constituents, and then precipitated gold, including the carrier, by hydrogen iodide in hydrochloric acid solution. Tellurium(VI) was used as a hold-back carrier, its reduction to tellurium(IV) promoting exchange with the active species. The centrifuged gold was washed free from chloride and then treated with nitric acid. The precipitate was dissolved in *aqua regia* and the precipitation and purification steps were repeated. The gold solution was treated with a silver nitrate carrier, the silver chloride removed, and iron(III) chloride was added with enough sodium hydroxide to give a slightly basic medium; prolonged contact in a basic medium promoted loss of hydrated gold oxide. Gold was again precipitated, purified, extracted with ethyl acetate and finally precipitated by hydrogen iodide. The collected gold was washed, dried and weighed on filter paper. Counting of the 2·69 d gold-198 was done in a proportional counter.

Ores

Much research has been done on determination of gold in ores by neutron activation. Bailey and Schuler[20] applied the technique to ores of the Witwatersrand system. The gold values for the ores were compared with values obtained by fire assay; a statistical evaluation resulting from a reconnaissance survey was included.

Standards to simulate the ore samples were prepared by adding known amounts of gold to silica powder, grinding the mixture in a mill, drying, and rolling for 10 days. The gold was added in hydrochloric acid solution or as the cyanide complex. Portions (200 mg) of both sample and standards were irradiated in the neutron pile at Harwell. The chemical separation involved sintering with sodium peroxide and subsequent dissolution in *aqua regia*. About 40 mg of gold foil were added as a carrier and the mixture was treated with *aqua regia* and evaporated, and the residue was dissolved in hydrochloric acid. Silica was removed by centrifugation and hold-back carriers were added to the filtrate. Gold was precipitated by magnesium, then dissolved, and finally isolated with ethyl acetate. Aliquots of the organic layer were used for the determination. Measurements at the 0·41 MeV photopeak of gold-198 reduced the effects of traces of radioactive impurities which could contaminate the isolated gold. To determine the chemical yield an aliquot of the ethyl acetate was treated with hydroquinone to remove the gold, which was subsequently weighed as the ignited metal.

Comparisons of counts from ore samples were made with counts for similar weights of the irradiated standards prepared from a ground mixture of silica and known amounts of gold. The radiochemical purity of the isolated gold was checked by an examination of the half-life and the energy spectrum.

The results obtained from duplicate samples of ore indicated rather poor precision and the authors suggest such sources of error as shielding effects, instrumental deficiencies, adsorption of gold by silica during dissolution procedures, and sampling errors resulting from the need to use small samples for irradiation (instead of the large samples required for fire assay).

It must be noted that in any such comparison of fire assay and a proposed new method for the determination of gold in ores one may claim similarity of values but not accuracy of determination; a statistical or reconnaissance survey to provide fire assay results does not of itself indicate accuracy of gold values. As indicated by the authors[20] there is the difficulty that comparisons of this type with neutron activation methods involve the problem of obtaining a representative sample. Depending on the identity of the mechanically mixed gold constituent, obtaining a representative sample can be the most critical step in a fire assay even with samples of about an assay ton. With the present neutron activation methods for ores, only 0·1–0·2 g of sample are needed and the sampling problem becomes correspondingly more difficult.

It may be noted also that the determination of chemical yield by precipitation from the ethyl acetate extract, used by Bailey and Schuler,[20] requires an effectively quantitative recovery of gold. Furthermore, the technique used to incorporate the gold carrier, particularly in the standards, is likely to lead to loss of precision and accuracy, and this is recognized by these authors. Their results for the gold content of the ores reflect the potential difficulties in the techniques used. There are wide variations in the duplicate values for a specific ore and the standards, as great as 50% for the former and 25% for the latter. One cannot accept the authors' conclusions that "comparable results were obtained" from the proposed method. However, in view of the inherent difficulties, the mean values for each ore are surprisingly similar to the average fire assay values.

Quartz and silicon

For the determination of gold in quartz Vobecký and Knotek[21] used 100–300 g samples and extracted with *aqua regia*. Aliquots of the solution were evaporated, and along with standards were

irradiated for 20 hr with a flux of $1{\cdot}5 \times 10^{13}$ neutrons.cm^{-2}.sec^{-1}. Gold carrier (2 mg) in the form of the chloride was added to the irradiated samples, followed by addition of 2*M* hydrochloric acid and extraction with ether, after which the standard was diluted to a concentration similar to that of the sample. Gamma measurements were made at 0·41 MeV over a period of 20 min. The purity of the counted sample was determined by measuring the half-life, which corresponded to that of gold-198. Extraction from 2*M* acid solution served to eliminate iron, arsenic and tellurium. The use of aliquots of the extracted gold solution meant that the quartz samples could be made large enough to be reasonably representative. The gold content was $7{\cdot}5 \times 10^{-6}$%.

An interesting and potentially useful activation method for the determination of gold, silver, cadmium, tantalum, rhenium and elements of group III of the periodic table, in high purity quartz and organic filter media, was recorded by Gleit *et al.*[22] The research was initiated to determine the minimum blank corrections to be used in a study of concentrations of trace elements in the atmosphere. The techniques applied to eliminate errors of contamination *etc.*, were such that the concentrations measured "may be the lowest ever determined by activation analysis; concentrations of less than 1 ppb* could be measured."

To avoid the dangers incident to exposure of the organic filtering media to irradiation, minimize volatility losses, and eliminate reagent contamination, the ashing process was accomplished by a stream of pure oxygen which had been excited by passage through an inductive field.

Gold standards were prepared by dissolving the metal in pure acids and diluting with conductivity water to give about 40 μg of gold/ml. Redistilled hydrochloric acid was used to convert the gold carrier into the complex salt. The standards, samples and blank quartz tubes were wrapped in quartz wool, transferred to aluminium cylinders, and irradiated for 4 days at an equivalent thermal neutron flux of 5×10^{13} neutrons.cm^{-2}.sec^{-1}. The capsules were then opened and the contents dissolved along with 20 mg of carrier. The chemical treatment involved a series of separations to isolate the gold, which was then purified by a method similar to that described by Cowan.[19] The activities of the 2·7 d gold-198 and the 3·18 d gold-199 were counted. The activities for the gold isotopes were separated by mathematical resolution of the two-component decay curve. Chemical yields were determined from gravimetric measurements of the recovered stable gold carrier. The relative error was considered to be less than 10%. The two principal sources of contamination were activities produced by activation of stable species in the quartz ampoules, and fission products arising from fissile species in the samples and ampoules. "Suprasil" ampoules were simultaneously irradiated and treated in the same way as the filtering media. Only a small fraction of the total gold activity was derived from the quartz ampoules. It is interesting that the authors suggest that a 30-fold variation in the gold values indicated the existence of particulate concentrations in the filtering media.

For the determination of gold and other impurities in silicon, James and Richards[23] used carriers to remove the commonly occurring impurities, scavenged with iron or aluminium hydroxide and arranged to produce a final precipitate of low formula weight in order to avoid excessive self-absorption and thus to increase the sensitivity. It is noteworthy that the authors preferred to use gravimetric methods even though 100% recovery was unnecessary. The results indicated gold values as low as 5×10^{-6} ppm.

There is interest in the work of Bemski and Struthers[24] who used activation methods to find that gold was introduced onto the surface of silicon during heat treatment at temperatures above 900° with a resulting change of the electrical characteristics of the silicon. Concentrations of 10^{14} atom/cm^3 in the bulk material were attained by heat treatment over the range 1100°–1300°. To confirm the conclusions based on the half-life and energy measurements, the authors used radiochemical separation with inactive carriers.

For the routine determination of some 40 elements including gold and platinum in ultra-pure silicon, Thompson *et al.*[25] used gamma-spectrometric and radiochemical methods. For gold the traces were of the order of 5×10^{-5} to 4×10^{-4} ppm and for platinum 9×10^{-4} to 2×10^{-3} ppm.

For the determination of gold in various siliceous raw materials by neutron activation Stefanov *et al.*[26] irradiated 0·05–0·5 g samples and standards for 3 hr at a flux of $2{\cdot}4 \times 10^{13}$ neutrons.cm^{-2}.sec^{-1}. The standards were prepared by adding gold solution to a filter paper and drying it under an infrared lamp. After irradiation the samples and standards were allowed to cool for 24 hr and those samples which resisted acid dissolution were dissolved with the aid of sodium peroxide. Carrier gold was added and nitric acid was removed by sulphuric acid. The dried sulphates were then treated with hold-back solutions of copper, sodium and potassium, or cobalt, zinc and manganese. The basic solution was centrifuged and the gold in the liquid extract was isolated with ethyl acetate. Finally, the organic layer was evaporated in the presence of hold-back carriers and gold was removed by hydroquinone. The filter paper with the gold was dried to constant weight under an infrared lamp.

With some modification the standards were similarly treated. Both the beta and gamma activities of the gold-198 were measured 30 hr after irradiation. The chemical yield for the sample was 45–75%

* This is the American billion, 10^9

and for the standards 94–95%. In view of the methods of separation used it would be interesting to have an explanation for the large discrepancies between the recoveries for the standards and samples.

The authors included a table in which the gold values obtained by an unstated chemical method were compared with the results from activation analysis. For the low values these were respectively $1{\cdot}1 \times 10^{-6}$ and $0{\cdot}87 \times 10^{-6}$ g and for the highest values $25{\cdot}4 \times 10^{-6}$ and $22{\cdot}75 \times 10^{-6}$ g. The associated impurities in the original samples were lead, zinc, copper, arsenic, manganese, silver, sodium, iron and magnesium. The purity of the separated gold was determined by decay measurements. To determine the sensitivity, samples were used in which no gold could be detected by either spectral or chemical methods. On a basis of a minimum count of 100 cpm and a background count of 50 cpm a sensitivity of $2{\cdot}8 \times 10^{-10}$ g of gold was expected. The error of measurements was about 24%.

For the determination of gold in dehydroceramics or lithium, potassium, aluminium silicates that had been neutron activated, Kudo[27] used a chemical separation which involved adjustment of the gold-198 solution to pH 3, reduction by hydrazine sulphate and the addition of *p*-dimethylaminobenzylidenerhodanine as a collector. The mixed precipitate was centrifuged and dissolved in *aqua regia*, and an aliquot of the solution was used for activity measurement with a gamma-ray spectrometer. More than 95% of 10 μg of gold could be removed along with silver and some copper. Zinc, EDTA or hydrogen fluoride did not interfere.

Gold in siliceous and cellulose acetate residues has been determined by measuring the gamma spectral peak at 0·41 MeV. Irradiation for 3 hr with a flux of 5×10^{11} neutrons.cm^{-2}.sec^{-1} was used with pure gold samples to obtain the calibration and gamma spectrum curves. The method was sensitive to 10^{-5}% of gold,[28] thus exceeding spectrographic and colorimetric methods in sensitivity by 2 orders of magnitude.

Rocks

In a study of the neutron activation methods for gold in rocks, Vincent and Crocket[29] disagreed with the assumption made by Vincent and Smales[30] and Goldberg and Brown[31] that errors due to self-shielding in the 5-mg fragments of gold foil (0·002 in. thick), irradiated as standards along with the rock samples, could be neglected.

Vincent and Crocket found that gross errors were introduced unless very small amounts of gold were irradiated as standards; their results showed that an evaporated acid solution containing a few micrograms of gold gave a specific activity some 37% higher than a gold foil 0·002 in. thick irradiated simultaneously at a flux of 10^{11} neutrons.cm^{-2}.sec^{-1}. The authors found no appreciable variation in activity with standards whose gold content did not exceed 10 μg. The standards were prepared by evaporating the strongly acid gold solutions in silica ampoules. It was assumed that in the rocks and mineral samples the traces of gold were so uniformly distributed that errors resulting from self-shielding were inappreciable; this conclusion found some support in the precision obtained with duplicate samples of widely differing weights. Errors resulting from the presence of platinum, which on irradiation could produce gold-199 with a half-life of 3·15 d, were considered unlikely.

Activation methods were used by De Grazia and Haskin[32] for the determination of gold in rocks in concentrations varying from 0·6 to 44 ppb*. About 0·3 μg of gold was detected. The procedure used was a modification of that proposed by Vincent and Smales.[30] Samples of 0·7–2·0 g obtained from ground portions weighing 15–20 g were irradiated at a flux of 5×10^{10} neutrons.cm^{-2}.sec^{-1} for 6–8 hr. Standards consisted of 1*M* hydrochloric acid containing 50 μg of gold and were irradiated along with the rock samples. The latter were then mixed with weighed gold powder, the mixtures fused in zirconium crucibles with sodium peroxide, and the melts dissolved in hydrochloric acid. Insolubles were discarded, presumably without examination. Ethyl acetate was used to extract the gold which was finally converted into metal. Standards were combined with gold carrier and treated in the same way. Chemical yields exceeded 85%. Counting was restricted to the 0·41 MeV peak of 2·69 d gold-198 by window adjustment, thus discriminating against the peaks at 0·208 and 0·158 MeV of gold-199 produced from the 30 min platinum-199. The authors acknowledged the difficulty in defining the error resulting from sampling difficulties for metals, such as gold, which sometimes occur in minute nuggets non-uniformly distributed throughout the sample.

For the determination of gold in ores without a radiochemical treatment Lobanov *et al.*[33] roasted the samples at 700–900° to eliminate the influence of the activated isotopes of associated volatile constituents. Gold in amounts of 0·1 g per ton could be determined and the average error was ±12%. Neutron activation methods for gold in igneous and sedimentary rocks were used by Perezhogin *et al.*[34] Samples (30 mg), packed in aluminium foil, were irradiated for 6 hr at a flux of $8{\cdot}7 \times 10^{14}$ neutrons.cm^{-2}.sec^{-1}. For increased selectivity the samples were irradiated in a cadmium block. The samples were dissolved in hydrofluoric, nitric and sulphuric acids and aliquots were used for the activity measurements.

* American billion (10^9)

Minerals

Mineral samples containing as little as 5×10^{-5}% of gold were used by Dvukhbabnaya *et al.*[35] whose method required no radiochemical separation. An error of 10% or less was achieved on the basis of the spectrum line at 0·41 MeV, provided the Compton background from sodium, arsenic and iron isotopes was less than the activity of the gold-198 peak. One hundred samples could be analysed simultaneously; a method for rhenium was also included.

In the determination of 5–10 ppm of gold in smaltite, Gauthier[36] activated 1-g samples of the mineral or of the mineral plus 10–15 μg of gold (as the chloride or as an ethyl acetate solution). The irradiated samples were combined with about 20 mg of carrier gold and treated with *aqua regia*. The filtered solution was treated with hydroquinone, the gold redissolved, and a second precipitation made; the gold was washed and weighed and its activity at 0·41 MeV was counted with a scintillation counter. Counting of the 0·97 MeV beta-rays was also possible but the former procedure was preferred. With a sample of smaltite the values found were 6·4 and 6·2 ppm, compared to 5·7 ppm by an unstated chemical method.

It may be suggested that the authors' method of mixing carrier and samples does not ensure homogeneity. Furthermore, it appears that the filtered residue was not examined for the presence of gold.

Meteorites

A radiometric determination of gold and rhenium in meteorites was used by Goldberg and Brown.[31] Measurements were made with the 2·7 d gold-198. Samples of the meteorites and gold standards were irradiated in the Argonne heavy-water pile, then dissolved in *aqua regia*; known amounts of gold carrier were added and, in the case of the meteorites only, gold was extracted with ethyl acetate and finally precipitated by hydroquinone. With the standard samples only the hydroquinone precipitation was applied. The ignited gold was weighed and the activity counted. The chemical yield averaged 75%. The effect of self-shadowing of samples and standards was examined. The gold content determined for two meteorite types varied widely from values previously recorded in the literature.

The published procedures for meteorites used by Goldberg and Brown were discussed by Vincent and Smales.[80] Vincent and Crocket[39] applied the method to the determination of gold in basalts, dunites and chondritic meteorites. The results showed excellent precision for concentrations of gold as low as 10^{-3} ppm.

Sea water

Gold in sea water containing as little as 3 to 5 μg/m^3 has been determined by neutron activation techniques. Hummel[37] believed that this sensitivity for the method could be increased further by a reduction in the values for blanks. Samples of sea water, and standards along with blank silica tubes were irradiated for 2–6 days and then left for 2 or 3 days to allow the activity to fall to a suitable working level. The irradiated sea water samples were transferred to beakers, standard carrier gold solution was added and the gold was isolated by repeated alternation of the solvent extraction with ethyl acetate and precipitation by hydroquinone described by Goldberg and Brown.[31] Finally the gold was weighed and counted. The irradiated standard gold solutions were similarly treated. The activities of the sea water samples were corrected for the mean activities of the tubes (about 7% of the sea water activities) and for coincidence, background, and chemical yield, the latter varying between 60 and 80%. The purity of the precipitated gold was examined by measuring 6–7 half-lives and indicated that only the 2·69 d isotope was present. The author was very careful in avoiding contamination. Presumably his use of neutron activation for the determination of gold in sea water was prompted by "the wide variations and uncertainties in much previous work, owing almost certainly to the difficulties inherent in the classical methods when extended to their lower limits." From the descriptions of the earlier analytical methods used it would seem that the choices of "classical methods" were, in general, unfortunate. The separational techniques now available do permit the application of conventional and proved methods of determination. Recently,[37a] anion-exchange separations for gold in sea water have been applied which allow determination of about 9 μg per ton of water with a concentration factor of about 2×10^7. In the light of the present uncertainties about the character or identity of the dissolved gold constituents, geological influence on gold content, and variations in gold content, it would seem that there is here a fertile field of investigation requiring both conventional and neutron activation methods of determination.

Organic material

Neutron activation determinations of gold in marine organisms have been reported.[38] For contents of 0·003–0·093 ppm the probable error was about ± 30%. About 500 mg of biological ash

and standards containing 7×10^{-9} to $2{\cdot}4 \times 10^{-7}$ g of gold in solution were added to filter paper, dried, and irradiated by a neutron flux of $2{\cdot}5 \times 10^{12}$ neutrons.cm^{-2}.sec^{-1} for 14·1 hr. The samples were cooled for about 5 days and gold was isolated by extraction with ethyl acetate and finally precipitated by sulphur dioxide. The gamma activity of gold-198 was measured at the 0·41 MeV photopeak. For standardization the activities were normalized to 10 hr radiation at a neutron flux of 1×10^{12} neutrons.cm^{-2}.sec^{-1}.

Neutron activation methods were also used by Fukai and Meinke[39] for the determination of gold, *etc.*, in marine biological ashes. The authors suggested the possibility of some loss during the ignition processes but presumably no direct measurement of any ignition loss was made. The maximum overall errors were estimated as ±30%.

Gibbons[40] recorded two neutron activation methods for the determination of gold in biological material. The rapid method, recommended when an error of 5–10% was acceptable, involving precipitation by magnesium, dissolution of the precipitate, addition of sodium chloride and ammonium phosphate as hold-back carriers, and finally precipitation by hydroquinone. The gold activity was determined by plotting a gamma-energy spectrum and measuring the area under the peak at 0·41 MeV, taking the extrapolated Compton response as the base line.

The second, less rapid, method involved cooling the irradiated sample for 24 hr, addition of carrier gold solution, treatment with acids to remove organic matter, addition of the hold-back carriers, precipitation by magnesium, extraction with ethyl acetate, three precipitations with hydroquinone, and drying the gold to constant weight. The irradiated standard gold solution was finally precipitated by hydroquinone. The method applied to liver containing 0·010–1 ppm of gold gave an error of about 2%.

The application of neutron activation to determining the distribution of gold in various animal tissues was discussed by Tobias and Dunn.[41] Ten μg of gold in the form of thiosulphate were injected into the tail vein of a mouse. Subsequently samples of various organs and tissues were wet-ashed and irradiated, after which the sample was dissolved in *aqua regia*, aliquots were treated with carrier, and the gold was separated by precipitation as metal. The activity of gold-198 was determined after electroplating on platinum discs. In determining the distribution the authors used a monitoring sample prepared by simultaneously irradiating a sample of gold chloride. The authors predicted useful applications of the technique in biochemistry, plant nutrition, pharmacology and toxicology.

Activation methods were also used by Tobias and Dunn[41] to determine the distribution of gold in human blood from leukemia patients. The blood was fractionated into plasma, and white and red cells, the ashes of which were irradiated. Only 10 ml of blood were required for the determination of gold in the white cells, whose total volume in the body was calculated to contain 14 μg of gold. Approaches to associated medical problems were clearly indicated by the finding that the relative activity induced in the white cells per mg of dry ash was about 10 times as high as that for red cells and 50 times as high as that for plasma.

For the determination of gold in blood, Purser *et al.*[42] added the sample to filter paper which was then activated in a flux of 10^{12} neutrons.cm^{-2}.sec^{-1} for 4 days. Activity measurements were made after about 6 days (to allow the decay of sodium activity). The samples were counted on a wide channel (12–32 V) and the phosphorus-32 background activity, which was relatively constant from sample to sample, was estimated from 10–15 samples that contained no gold.

For the determination of gold in liver tissue, Raković[43] evaluated the method by adding 1 μg of gold to the organic tissues. These and standard gold samples, in which gold was deposited on filter paper, were irradiated for 48 hr at a flux of $1{\cdot}5 \times 10^{12}$ neutrons.cm^{-2}.sec^{-1}. After irradiation the samples were mixed with 60 mg of gold carrier, and 30% hydrogen peroxide, sulphuric, nitric and perchloric acids were added to destroy organic matter. *Aqua regia* was used to dissolve the gold, the salt was converted into chloride, and then dilute sulphuric acid and a hold-back carrier containing potassium and sodium chlorides and phosphates were added. Finally the gold was precipitated twice with oxalic acid, heated and weighed to determine the yield, and then beta-counted with an end-window Geiger-Mueller tube. The chemical yield for 6 samples each containing 1 μg of active gold varied from about 21 to 30%. This low yield could be expected with oxalic acid as the reductant. The weighed gold was found to be radiochemically pure. The impurities in the irradiated organic samples to which no gold was added produced 0·09–0·26% of the count rate measured for 1 mg of gold. The sensitivity of the method is limited primarily by the impurities. The author's results indicated that with 10^{-7} g of gold a precision of 5% could be achieved.

Vacik and Christian[44] recorded an activation method for determining 20–250 μg of gold per g of biological samples, which required no chemical separations and allowed direct qualitative and quantitative gamma-ray measurements. Samples and standards, the latter containing known amounts of gold chloride or gold thioglucose and liver tissue, were irradiated for 1 hr at a flux of 2×10^{9} neutrons.cm^{-2}.sec^{-1} and the activity was measured, after 12 hr decay, at the 0·41 MeV peak of gold-198 with a 3-V window. The potential interferences from the 15 hr sodium and from other

constituents normally found after tissue activation were avoided by the 12-hr cooling period and comparisons with standards indicated that only gold-198 provided the measured activity. The authors stated that by increasing the flux or the period of exposure the sensitivity could be increased to 1 μg of gold.

Alloys and metals

Copper. Nakai *et al.*[45] determined gold, manganese and sodium in copper metal. Irradiations of 200 mg of sample and standards were made with a flux of 3×10^{11} neutrons.cm^{-2}.sec^{-1} for 2 hr. The sample was dissolved and gold was extracted from the chloride solution with ethyl acetate. Copper and manganese were removed as sulphides and sodium was collected in the filtrate. For the determination the author used the gamma spectra of gold-198, manganese-56, and sodium-24.

To determine gold in electrolytic copper, Hirano *et al.*[46] separated copper before irradiation, to eliminate the radioactivity of copper-64. Gold was retained on an anion-exchange column of Amberlite IRA-400 and the resin was irradiated together with standards for 4–5 hr with a flux of 4×10^{11} neutrons.cm^{-2}.sec^{-1}. The residue was ashed and the gold-198 extracted with ethyl acetate and measured by gamma-ray spectroscopy. Correction for losses was considered unnecessary and good precision was obtained at the 0·01 ppm level.

Gold was determined non-destructively in copper-gold mixtures by Okada and Kamemoto.[47] In contrast to the flux of 2×10^{8} neutrons.cm^{-2}.sec^{-1} used by Anders[48] the authors used a flux of 3×10^{11} neutrons.cm^{-2}.sec^{-1}. Samples (12 mg) of mixtures containing about 90% copper and 10% gold were irradiated for 4·5 sec, cooled for 5 sec, counted for 5 sec, again cooled for 1 sec and counted for 5 sec. A sodium iodide scintillation detector and multichannel analyser were used to measure the 0·279 MeV gamma rays. Beta rays from the sample were absorbed by an aluminium disc. The active isotope was identified as gold-197m.

An extensive neutron activation analysis of the trace constituents in high purity copper was described by Cuypers.[49] Silver and nitric acid were removed successively, selenium was added, gold was reduced by hydrazine hydrochloride and carried down by the selenium. The gamma activity of gold-198 at 0·411 MeV was then measured.

Lead. Traces of gold and arsenic in high purity lead were determined by Hirano *et al.*[50] by irradiation in a flux of 7×10^{11} neutrons.cm^{-2}.sec^{-1} for 7 hr. The subsequent chemical separation involved addition of carriers, precipitation of lead sulphate, extraction of gold by ethyl acetate, distillation of arsenic and reduction of gold and arsenic. Chemical yields varied between 60 and 100%. The purity of precipitates was checked by measuring the decay rate and the maximum energy of the emitted beta particles. The error was stated as $\pm 10\%$.

Lead, bismuth, copper and zinc. Substoichiometric methods for the determination of traces of gold in lead, bismuth, copper and zinc were used by Alimarin and Perezhogin.[50a] The aurate ion in a wide range of mineral acid concentrations formed chloroform-soluble precipitates with tetraphenylarsonium chloride. The various coextracted elements, which included osmium in concentrations comparable to those of gold, did not interfere. There was no interference from up to 1 g of the primary base metals. The test samples, properly cleaned, together with standards of about 1 μg of gold deposited on filter paper, were irradiated for 20 hr at $8·7 \times 10^{12}$ neutrons.cm^{-2}.sec^{-1}, and cooled for 1 day for lead and bismuth, and 6–7 days for copper and zinc. Bismuth, copper and zinc in the presence of gold carrier were dissolved in nitric and hydrochloric acids. Lead with gold carrier was dissolved in nitric acid, hydrochloric acid was added and lead chloride was filtered off after an evaporation and addition of hydrochloric acid. The acid solutions of the base metals were evaporated almost to dryness, hydrochloric acid and 1 ml of 0·003*M* tetraphenylarsonium chloride were added and the whole shaken with 2 ml of purified chloroform. The extract was centrifuged and 1·5-ml aliquots were used for activity measurements of gold-198 at 0·41 MeV. The irradiated gold standards were dissolved in *aqua regia*, then an aliquot containing about 1×10^{-8} g of gold was mixed with carrier, and the tetraphenylarsonium chloroaurate was extracted with 2 ml of chloroform and the rest of the procedure used for the sample was applied. The authors were able to determine 5×10^{-11} g of gold with an error of $\pm 5\%$.

Beryllium. For the determination of gold and other trace impurities in beryllium, Negina and Zamyatnina[51] used extraction from hydrochloric acid solutions with diethyldithiocarbamate in chloroform. The extract was evaporated and the dry residue was dissolved in hydrochloric acid and treated to form sulphides which were then dissolved in hydrogen peroxide and concentrated hydrochloric acid. Gold was then isolated with diethyl ether. The test element and standard were prepared in the same gravimetric form and placed on the targets used for measurement. Standardizing the amounts on the target and the measuring conditions avoided the need for self-absorption and self-scattering corrections. Decay curves were used to indicate radioactive purity.

Platinum. Traces of gold in platinum have been determined by neutron activation techniques.[52] Samples and standards, the latter containing added gold, were irradiated for 2·5 hr with a neutron

flux of 8×10^{11} neutrons.cm^{-2}.sec^{-1}. The activity of gold-198 was measured by a discriminating gamma-counting method which avoided measuring the activity of gold-199 produced simultaneously by the reactions ^{198}Au(n, γ) ^{199}Au and ^{198}Pt(n, γ) ^{199}Pt $\xrightarrow{\beta^-}$ ^{199}Au. Interference from gold-198 produced from plantinum-196 could be neglected under the conditions used for the method. The transferred irradiated samples and standards were treated with carrier gold and *aqua regia*. The gold was extracted with ether, precipitated by hydroquinone, redissolved, extracted with ethyl acetate, finally precipitated by hydroquinone and weighed, and its activity was then counted.

The counting rates were corrected for background, for any significant decay between counting the samples and standards, and for chemical yield, which was about 75%. The gamma-ray spectrum of the precipitated gold indicated the absence of interference from gold-199. Decay measurements showed that only the activity of gold-198 was being measured. The gold content of various platinum samples ranged from 0·6 to 3·6 ppm. It was stated by the authors that the full sensitivity for gold is not realised in determinations in platinum, because of nuclear complications, but as little as 0·1 ppm of gold could be determined by their method, giving about 50 cpm above the background count.

Impurities in gold

For the determination of traces of cobalt, copper, tellurium, arsenic and antimony in gold, Yakovlev *et al.*[53] irradiated 200-mg samples and standards in a neutron flux of 5×10^{12} neutrons.cm^{-2}.sec^{-1} for 48 hr. Carriers were added, the samples were dissolved in *aqua regia*, and gold and tellurium were precipitated by sulphur dioxide and hydrazine. The precipitate was treated with concentrated nitric acid, gold was extracted by ether from 8*M* hydrochloric acid, and finally precipitated by hydroquinone. Details were given for the determination of impurities in the concentration range of about 10^{-5}–10^{-6}%. The error was ±10–15%.

Neutron activation methods were used by Yajima *et al.*[54] to determine trace impurities of copper, arsenic and antimony in gold and silver. Irradiation was made in a flux of 3×10^{11} neutrons.cm^{-2}.sec^{-1} for 1 or 3 days. The irradiated gold was dissolved in *aqua regia* and extracted with ethyl acetate. The nuclides measured were palladium-109, copper-64, arsenic-76, antimony-122 and gold-198.

General methods for gold

The relatively new and potentially useful technique of substoichiometric extraction for determination of gold traces was recorded by Beardsley *et al.*[55] Gold solutions in sulphuric or hydrochloric acid were treated with an known constant amount of copper diethyldithiocarbamate that was insufficient for a complete replacement of the copper in the complex by gold. The gold complex was then extracted with chloroform and the activity of a measured aliquot of the chloroform extract from the test sample was compared with that of the same amount of extract from a standard, both samples and standards containing carrier gold labelled with gold-198.

Methods such as these can be applied to avoid extensive radiochemical separation and can be highly selective provided appropriate extraction systems are available.

The method will be useful for determinations made on materials whose compositions are known with some certainty. On the other hand, at least as far as gold in ores, rocks, *etc.*, is concerned, there will be the problem of some uncertainty as to the presence of constituents which are potentially interfering. Although it is easy to find what the composition is by spectrochemical techniques, it is doubtful whether substoichiometric methods, as presently proposed, provide any significant advantages over the very simple radiochemical separation available for gold in complex ore materials.

The authors investigated interference by a variety of associated metals and of the acid media normally required for dissolution of samples, either indirectly by detection of any depression of the gold activity of the extract caused by the addition of various metal ions to the test solution, or directly by adding microgram or submicrogram amounts of radioisotopes of the ions concerned. There was interference from palladium and tin, that of the latter being avoided in the proposed procedure by the use of hydrogen peroxide.

It is unfortunate that the techniques used to identify interfering constituents did not include investigation of the dissolution processes. One cannot assume that foreign constituents added after dissolution would form the same species as they would if added before the dissolution procedure. While it may seem unlikely that there would be an adverse effect on the extraction procedure, experience with similar influences in spectrophotometric techniques sounds a warning note.

It is of interest to note that platinum was coextracted with gold, but presumably by a different mechanism. In any case, except for a very small contribution from the 0·28 MeV gamma ray of platinum-197, interference can be avoided. The authors investigated the effects of acidity, time required for extraction equilibria, and variations in proportions of gold carrier solutions. The permissible range of acidity was 0·01–10*N* sulphuric or hydrochloric acid and reaction equilibrium was reached within 20 sec. Dissolution procedures were provided for biological material, lead, silicon and rocks. Losses of gold during dissolution were investigated using a non-irradiated matrix

and a known amount of active gold. The losses for silicon, lead and kale were 6, 4 and 6% respectively.

Emery and Leddicotte[56] have discussed the analytical chemistry of gold, counting techniques, safety practices, *etc.*, and have given a collection of detailed radiochemical procedures. This report is a useful compilation of the carrier-free and carrier-separation techniques, types of nuclear bombardment, types of material analysed, separation time, and evaluations of the usefulness of the procedures for freeing radioactive gold isotopes from contamination with other radioactive species. The authors note that for the determination of gold in biological material the procedures of Tobias and Dunn[41] and of Gibbons[40] are usually applied, and for the analysis of meteoritic material the procedures proposed by Goldberg and Brown[51] and by Smales[57] are frequently used.

An interesting application of radioactive gold to analytical techniques was described by Pompowski and Szponar.[58] These authors used gold-198 to study migration phenomena in paper electrophoresis and chromatography. The results indicated that planimetry wax was not suitable for quantitative work.

Uranium. Abrao[59] used activation methods for the simultaneous determination of gold and uranium, over the range 18–23 ppm of gold.

The application of a neutron activation method for gold in diamond was recorded by Freedman.[60] After irradiation with a pile neutron source for 8 hr 1–2 μg of gold were found in a 100-mg sample of diamond. Its presence as a surface contaminant was discounted.

Ruthenium

It has been stated in reports dealing with the determination of osmium or ruthenium in submicrogram amounts that only neutron activation methods are sufficiently sensitivite. It may be that this attitude, which is without validity, has discouraged attempts to establish the accuracy of the activation methods. Although some comparisons have been made with spectrochemical methods, these comparisons are not valid unless the accuracy of the spectrochemical methods has also been proven. The spectrochemical methods are not the only established methods available for such comparisons.

Platinum

Killick and Morris[61] recorded a method of determining traces of ruthenium in platinum by a neutron-activation method together with the comments that with the samples used, no ruthenium could be detected by emission spectrographic analysis and that the limits of sensitivity exceeded those of most other analytical methods. These statements leave the inference that other analytical methods are inapplicable to the range of 1–2 ppm of ruthenium to which the authors applied their method. Both osmium and ruthenium can be so easily concentrated by distillation or solvent extraction that the sensitivities of most spectrophotometric reagents for them lie within the range of most published activation methods and there is thus available a most effective method of evaluating the relative accuracy of activation methods.

Killick and Morris[61] used thermal neutrons to activate samples of platinum together with standards made by adding powdered platinum to standard ruthenium solutions and evaporating to dryness. After activation the samples were dissolved in concentrated hydrochloric acid together with ruthenium carrier prepared from ruthenium(III) chloride. Nitric acid was added, and after dissolution was complete and nitric acid had been removed by evaporation, the hydrochloric acid solution was treated with osmium carrier, fumed with sulphuric acid, treated successively with potassium permanganate, iron(II) ammonium sulphate, nitric acid and then carbon tetrachloride to extract the osmium. The ruthenium in the aqueous phase was oxidized by silver(II) oxide and the octavalent oxide was extracted with carbon tetrachloride and back-extracted into sodium hydroxide and dithionite solution. A gold salt was added as a scavenger and ruthenium was finally precipitated as the hydrated oxide by methanol, and the activity of this form was counted. The chemical yield was determined by dissolving the ruthenium oxide, quantitatively oxidizing, and finally measuring the absorbance as for the carrier solution. The radiochemical purity of the ruthenium was checked by the usual methods. Counting rates were corrected for paralysis, background, chemical yield, and any significant decay differences between samples and standards. Interferences from the radionuclides content ranged from 0·83 to 1·96 ppm.

A method of distillation of carrier-free ruthenium by oxidation with lead(IV) oxide instead of peroxysulphate was described by Kanbara *et al.*[62] The tetroxide was collected in an aqueous solution of small amounts of nitric acid and hydrogen peroxide. The ruthenium in the distillate was coprecipitated with iron(III) hydroxide. The lead oxide was considered a more effective oxidant than peroxysulphate or permanganate.

Sea water

Radio-ruthenium in effluent and sea water was determined by Loveridge and Thomas[63] on aliquots of one litre. The procedure involved addition of ruthenium carrier, potassium peroxysulphate, potassium hydroxide, and potassium periodate. Radiochemical exchange was achieved

by heating at or near the boiling point for a few min. The resulting solution was cooled and slightly acidified, and the tetroxide was extracted by carbon tetrachloride. Methanol was used to precipitate ruthenium oxides from the organic phase. These were washed and transferred to an aluminium tray and beta-counted. The oxides were then dissolved in alkaline periodate and the chemical yield determined spectrophotometrically. The carrier solution was prepared from ruthenium trichloride by precipitation with methanol from a solution containing sodium hydroxide and potassium peroxysulphate, and re-dissolved in the latter media. The effectiveness of recovery from sea water and effluent was tested with ruthenium-106 tracer; overall recovery of 99% ± 2·5%, corrected for the chemical yield of the added carrier, was obtained. The efficiency of the chemical method of separation used by the authors may be measured by the recovery of the carrier. By weight the recoveries varied from 72 to 87%; by spectrophotometric measurements the range was 70–83%. The extent of interference from other possible fission products was acceptably small. Improved purity could be achieved by dissolution of the ruthenium oxide precipitate and treatment with a zirconium carrier.[64]

For the analysis of the effluent and of sea water the beta activity of the isotopic pair, ^{106}Ru-^{106}Rh was used as the reference standard and other Ru-Rh pairs were counted as if they were this pair. However, the weak beta particles of ruthenium-106 were screened by the use of a thin aluminium absorber, which restricted the beta counts to those of rhodium-106. The thin ruthenium oxide source caused little absorption of the rhodium activity and the results indicated that no correction for back-scatter was required.

Fission products

To determine ruthenium activity in a solution of the fission products of irradiated plutonium, Meadows and Matlock[9] took an aliquot of the solution in a separatory funnel, added ruthenium and zirconium carriers, concentrated sodium hydroxide solution, a solution of sodium hypochlorite, and hydrochloric acid to a pH of 4, and finally extracted the ruthenium tetroxide with re-distilled carbon tetrachloride. After an aqueous wash, the ruthenium was back-extracted from the carbon tetrachloride with sodium hydroxide solution containing sodium bisulphite. Ruthenium was precipitated from an aliquot of the alkaline solution by ethanol and filtered, and the activity was finally counted. The carrier ruthenium used in the method was standardized by precipitation with magnesium powder, and used for the spectrophotometric calibration curve needed for determination of the chemical yield. Because the fission-product ruthenium was not oxidized as rapidly as the carrier-ruthenium the isotopic exchange, after oxidation by the hypochlorite, was encouraged by allowing 1 hr for the oxidation. As might be expected there was some evidence of loss of ruthenium tetroxide immediately following the adjustment of acidity before the extraction.

The authors stated that "as in other radiochemical methods, 100% yield is not required so long as the yield of each sample is measured and the count rate is corrected for that yield." While this statement is acceptable with reservations, some of which were discussed in the introduction to this review, the authors' failure to recognize the significance of their technique is noted. The method used by the authors for determining the chemical yield does require an analytically complete recovery of the ruthenium by ethanol. This condition could have been avoided had the authors made a direct recovery determination, perhaps by reduction, of the oxide which was used for counting. It may be noted that the accuracy of the ethanol and the magnesium precipitation methods for ruthenium has not been proven analytically.

Rickard and Wyatt[64] recorded a radiochemical non-distillation method for the determination of ruthenium in aqueous solutions of fission products. The procedure required treatment of the fission solution with solutions of ruthenium carrier, sodium hydroxide, potassium periodate and sodium hypochlorite. Zirconium carrier was used to remove extraneous constituents and then the ruthenium was repeatedly precipitated by magnesium and by ethanol, and finally the ruthenium was reduced by magnesium, purified, transferred to a filter paper, washed, dried, and weighed, and its activity was counted. The accuracy compared favourably with that obtained by distillation of the ruthenium.

To separate radio-ruthenium from other fission products, Melnick modified the method used by Glendenin.[19] The tetroxide was distilled from a solution of perchloric acid, sodium bismuthate and fuming nitric acid. The solution of the sample containing the ruthenium carrier, the oxidants, and phosphoric acid to prevent volatilization of molybdenum, was heated to distil the tetroxide, which was collected in 6*M* sodium hydroxide solution from which hydrated oxides of ruthenium were then precipitated by ethanol. The oxides were dissolved in hydrochloric acid and the metal was then precipitated by magnesium and collected on filter paper, washed, dried, and weighed, and its activity was counted. The chemical yield was about 70%; duplicate analyses required about 3 hr. The 42 d ruthenium-103 was separated from the 106-isotope or determined in its presence by the use of a scintillation counter and an aluminium absorber to eliminate the 3·55 MeV beta ray from the 106-isotope. The latter may be counted on a beta proportional counter using an aluminium absorber to cut out the 0·68 MeV beta ray of ruthenium-103.

As part of a scheme for separating useful products from uranium fission Brezhneva *et al.*[65] separated ruthenium from the supernatant liquid of a calcium oxalate precipitation by the use of nickel sulphide which carried down 80% of the ruthenium. After dissolution of the sulphide, ruthenium was extracted from the nitric acid solution by tributyl phosphate; 99·0% could be extracted under optimum conditions.

Osmium

Meteorites

For the activation determination of osmium and rhenium in meteorites, silica, *etc.*, Morgan[66] combined a variety of procedural innovations for chemical recoveries. Here, as with all similar activation applications, these innovations will not necessarily be applicable to quantitative analysis. It is perhaps unfortunate that little, if any, of such work includes results which would indicate that a proper attempt was made to evaluate critically techniques that are fundamentally suspect; a chemical yield determination is not always an adequate substitute for such an evaluation. A case in point is Morgan's[66] assumption that exposure of irradiated meteorites to air before chemical treatment is unlikely to result in any significant loss of osmium. While this may be so in specific instances, such an assumption can and ought to be supported experimentally, particularly when nanogram amounts of osmium are to be determined. The method of preparing standards chosen by Morgan[66] involved the addition of a standard osmium solution to 20–30 mg of Specpure silica in a dry silica ampoule which was reweighed, centrifuged, dried at 80° overnight, sealed and irradiated. In the present authors' opinion, based partly on an accumulation of experimental data, this approach to the preparation of irradiation standards is not acceptable without some experimental support. In the case of osmium and most other noble metals such evidence may readily be obtained by applying the method to similar complex material of which the osmium content has been determined by proven procedures. The ease of selective isolation of fractions of micrograms of osmium from gram samples of materials such as the chrondrites used by Morgan, allows a ready evaluation of the activation method.

The chemical separation of osmium and rhenium used by Morgan[66] involved the use of an anion-exchanger and elution with nitric acid solutions. This method, now being studied by the present authors, has not been developed analytically and it would be of considerable interest to know the results which supported the statements that the "anion-exchange behaviour of osmium depended on the number of chloride ions in the anionic complex" and that "virtually quantitative elution of osmium could be achieved with 0·8*N* nitric acid provided that the flow-rate was reduced to 0·25–0·5 ml/min and not more than 5 mg of osmium carrier was used."

Rock samples (0·1–0·2 g) along with standards were irradiated at a thermal flux of 9×10^{12} neutrons.cm^{-2}.sec^{-1} for 1 week and then allowed to stand for about 24 hr. The sample was transferred to a zirconium crucible and carrier solution prepared from ammonium hexachloro-osmate was added, followed by ethanol to prevent loss of osmium tetroxide. Sodium hydroxide was added to provide a medium for complete isotopic exchange. The mixture was dried, sodium hydroxide was added, and heat carefully applied; the fused mixture was cooled, sodium peroxide was added, and the fusion was completed. The cooled fused residue was dissolved and transferred to a beaker and centrifuged to isolate base metal oxides. The supernatant liquid was treated with ethanol and hydrochloric acid and filtered to remove silica. The filtrate was passed through a small amount of De-acidite FF anion-exchanger to isolate osmium and rhenium, and osmium was selectively eluted with 0·8*M* nitric acid at the required flow-rate of 20–30 ml/hr. The eluate was drained into a sodium hydroxide solution to which ethanol was added. Finally the osmium was precipitated as the hydrated oxide, which was treated first with phosphoric and sulphuric acids and then with permanganate, the excess of which was removed with iron(II) ammonium sulphate; then cold nitric acid was added and the osmium tetroxide was extracted with chloroform. After back-extraction into thiourea-hydrochloric acid solution, osmium was precipitated by potassium chromithiocyanate and the precipitate was dried and weighed. The chemical yield varied between 30 and 60%.

The standards were prepared as described above and given a similar chemical treatment.

The beta count-rate of osmium-191 was corrected for dead time losses, background, and self-absorption loss, the last determined empirically. The validity of the self-absorption correction was checked by determination of the gamma ray activity of the 0·646 MeV photopeak of osmium-185. Interference from self-shielding and from the osmium radionuclides resulting from iridium and platinum was considered to be negligible. Results on various chondrites vary between 0·3 and 0·9 ppm; values which are within the applicable range of standard osmium methods.

For the determination of osmium and rhenium in iron meteorites Herr *et al.*[67] used cleaned compact pieces weighing 1–2 g and irradiated for 3 days at a flux of 10^{13} neutrons.cm^{-2}.sec^{-1}. After exposure the chips were cleaned in nitric acid and weighed. For the activity measurements osmium-193 was used and in some cases osmium-191 was used as a control. The standard of pure potassium chloro-osmate was activated with the sample and carried through the determination described

below. For osmium determinations the samples and standards were dissolved in sulphuric acid containing potassium hexachloro-osmate. After a 2 hr dissolution period the osmium tetroxide was distilled from chromium(VI) oxide solution and collected in hydrochloric acid containing thiourea. This solution was concentrated and the tetroxide distilled from a sulphuric acid–chromic oxide solution and collected in a sulphur dioxide–hydrochloric acid solution. The osmium was again removed by passing a current of air through the boiling solution, and collected in a thiourea-hydrochloric acid solution. This final treatment removed interference from ruthenium and other elements. The chemical yield was determined spectrophotometrically and was 60–70%. The osmium values for 10 iron meteorites varied from about 0·6 to 3·2 ppm, which would permit the application of direct spectrophotometric osmium determinations.

Ruthenium

Neutron activation methods have been used to determine traces of osmium in ruthenium sponge. Gijbels and Hoste[68] isolated the osmium by distillation from a sulphuric acid–hydrogen peroxide solution. Use was made of 16 d osmium-191, the samples being processed about 14 days after irradiation for 3–5 days at a neutron flux of $4{\cdot}8 \times 10^{11}$ neutrons.cm^{-2}.sec^{-1}. In ruthenium samples irradiated and processed under the same conditions, the main activity is caused by the 41 d 103-isotope. The efficiency of separation was determined with tracers either alone or in the presence of 1–10 mg of osmium or ruthenium carrier. In the latter case the solution of tracers was added to the carrier sponge, then the mixture was evaporated, and the residue was fused with sodium peroxide and transferred to the distillation flask with water and acids. The distillate from the sulphuric acid and hydrogen peroxide mixture was collected in sodium hydroxide solution and diluted to standard volume, and the activities of both distillate and pot liquid were measured by a gamma scintillation counter with a pulse-height analyser to eliminate the activity of rhodium-105. The material balance fitted within 2%.

The ruthenium contamination of the osmium distillate both with and without carriers was less than 0·01% of the total ruthenium activity. The authors noted the beneficial effects on the separation if the solution was aged for several hours before distillation. However, with increasing size of the ruthenium sample there was an increase in the degree of contamination. Examination of the distillate showed that the osmium was contaminated by a small and fairly reproducible amount of ruthenium interference. If the osmium content is low the interference can thus become significant. This should be remembered when applying established methods of separating and determining osmium and ruthenium.

Ruthenium interference was appreciably reduced by use of a 3 in. × 1 mm wafer instead of a 3 in. × 3 in. detector. With the latter a correction for the ruthenium content of the osmium distillate is required when the osmium content of the sample is less than 30 ppm; with the wafer, only when the osmium content is below 10 ppm. The addition method of analysis was used, and the standard deviation was determined from the slope and the intercept with the ordinate. For a commercial ruthenium sponge the osmium value was approximately 17 ppm, for spectrographically pure ruthenium 33 ppm, and for a sample prepared by the authors about 1·7 ppm. There was good agreement between values obtained by the use of the wafer and the crystal.

Gijbels and Hoste extended this investigation[68] to include the determination of ruthenium and iridium in osmium sponge.[69] Carriers were not required. The initial chemical separations used by the authors were analytically acceptable methods but the results obtained were surprisingly unpredictable. The method for isolation of osmium by acid-peroxide distillation used previously by the authors[68] removed 99·8% of the osmium. The residual osmium in the pot liquid resisted continued distillation and although the classical treatment of the pot liquid with perchloric acid removed most of the residual osmium and all of the ruthenium an examination of the ruthenium distillate indicated distillation of traces of iridium. Thus the osmium and iridium contamination in the distillate was so high that ruthenium could not be detected in the osmium sponge. These findings are of exceptional importance in view of the fact that distillation from perchloric acid solution has been an accepted method of separating ruthenium from iridium. Fortunately, the authors will record the result of further researches dealing with the problem of co-distillation of iridium. Because of these difficulties the separational procedures were varied to include the usual osmium distillation with sulphuric acid and hydrogen peroxide, followed by an interim destruction of peroxide by the addition of potassium permanganate, then a continuation of the acid-peroxide distillation. Ruthenium was then removed by distillation from a sulphuric acid–sodium bromate medium. It may be noted that in some instances there remained a slight but not unexpected contamination from osmium. The proposed procedure was applied to the samples of osmium sponge and the addition method of analysis was again used. The addition method provided better results than the usual technique when amounts of ruthenium and iridium up to 3–7 times the original content were added to the sample.

For the analysis 10 samples of sponges were used to which were added known amounts of ruthenium and iridium on filter papers. The samples were irradiated for 3–7 days at a neutron flux of

4×10^{11} neutrons.cm^{-2}.sec^{-1}. The contents of the container were fused in a nickel crucible with sodium peroxide.* The fused melt was treated to remove osmium. The sodium hydroxide receiving solution contained 99·999–99·9999% of the osmium content of the ruthenium. Treatment of the pot liquid with sulphuric acid-sodium bromate removed more than 99% of the ruthenium activity and the residual pot liquid contained 99·995% of the iridium content of the sample.

A correction was required for the small amount of osmium contamination in the ruthenium distillate especially when the ruthenium activity was very low.

The radionuclides used for the determinations a few days after irradiation were osmium-191 and -185 (16 d and 93·6 d respectively), ruthenium-193 (39·8 d) and iridium-192 (74·4 d). The gamma-spectra of these isotopes were measured with a 3 in. × 3 in. NaI (Tl) detector. Activities of other constituents such as gold-198 could be neglected if measurements were made 2 or 3 weeks after the end of irradiation.

The results gave an iridium content of about 21 ppm in commercial osmium, about 1·5 ppm for spectrographically pure osmium, and about 0·5 ppm for a purified osmium sample.

The authors concluded that the neutron activation method applied to 10-mg samples allowed determinations of ruthenium down to about 10 ppm and iridium down to 0·5 ppm. In the opinion of the present authors the determination of traces of platinum metals in samples of osmium or ruthenium sponge by these neutron-activation methods provides no improvement in sensitivity or accuracy over applicable spectrophotometric methods.

Rhodium

A method of determining rhodium by thermal neutron activation was described by Steele and Meinke.[70] From the various neutron reactions, the authors selected the reaction ^{103}Rh (n, γ) ^{104}Rh + ^{104m}Rh for the determination. The rhodium-104, with a half life of 44 sec was used for a non-destructive method and the equilibrated species of rhodium-104 and -104m with an effective half life of 4·4 min, for a destructive method. The average time required for a determination by the former method was 7 min and by the latter about 20 min.

Irradiation fluxes varied from $9{\cdot}9 \times 10^{11}$ to $1{\cdot}3 \times 10^{12}$ neutrons.cm^{-2}.sec^{-1} but the results were normalized to a flux of 10^{12} neutrons.cm^{-2}sec^{-1}. For the non-destructive method the time elapsed from the end of irradiation to the start of the counting period varied from 19 to 54 sec. Counts were corrected for decay and analyser dead time, and background radiation from other activities was eliminated by extrapolation of the base line under the photopeak of 0·56-MeV.

Calibration data for the non-destructive determination of rhodium were obtained by 42-sec irradiations of known amounts of rhodium and subsequent determination through the gamma-ray scintillation spectra. The method was accurate to within about ±6% over the weight range 0·1–1 μg of rhodium. For the range 0·01–0·1 μg the error was about ±20%. In the presence of the halogens, tungsten, arsenic, antimony, copper, zinc and other elements with gamma peaks near 0·56 MeV, there may be interference, and a chemical separation is then required. The authors predicted that activation analysis of rhodium using the high energy beta-ray of rhodium-104 would improve the sensitivity.

The destructive method for rhodium-104m required heating the irradiated samples with sodium peroxide, dissolving the products in hydrochloric acid, treating with sodium hydroxide, adding rhodium chloride carrier, tartaric acid, and pyridine, and filtering into a separatory funnel and rinsing with hydrochloric acid. The solution was made basic with sodium hydroxide and the pyridine-rhodium layer was separated. Gamma-ray measurements were made on an aliquot. The chemical yield was determined by measuring the absorbance at 440 mμ of the pyridine-rhodium complex. The counts at the 0·56 MeV photopeak were corrected for decay, analyser dead-time, neutron flux variations, and the chemical yield. A calibration curve was prepared by this separation technique. The error of the method was about ±20% over the range 0·10–1 μg of rhodium. The average time for the determination was about 20 min including the 5 min irradiation time.

For the determination of radio-rhodium, Gilmore[19] used a procedure involving reactions which merit investigation with a view to analytical application. In successive stages of separation rhodium was precipitated as the iodide (RhI_3), then as the complex $Cu_3[Rh(CN)_6]_2$), and finally by electro-plating, the last method also being used for standardization.

The chemical separation involved addition of rhodium carrier, fuming the solution of nitric, perchloric and sulphuric acids to remove ruthenium, addition of perchloric and hydrochloric acids, addition of molybdenum and cobalt carriers and potassium iodide, and a separation of rhodium(III) iodide. The precipitate was dissolved in potassium cyanide, tellurium carrier was added and dissolved iodine was removed by sodium nitrite. The solution was scavenged with an iron salt in ammoniacal medium and treated successively with barium, tellurium, and antimony carriers, in a sulphide solution.

* Attention is drawn to the authors' use of a filter paper and its fusion with sodium peroxide. This technique may result in a violent explosion.

Copper nitrate was added to isolate the copper-rhodium complex, which was then dissolved, and the rhodium cyanide complex anion $[Rh(CN)_6]^{-3}$ was isolated and dissolved in sulphuric acid. After some repetition of separational steps, the rhodium was plated out on a weighed platinum disc. The cathode deposit was cleaned, weighed, mounted, and beta-counted. The chemical yield was about 60% and 6 determinations per day could be made.

Ruthenium

Rhodium in C. P. ruthenium metal was determined by activation analysis without the use of a chemical separation.[71] Samples (500 mg) were irradiated for 5 sec at a flux of $1{\cdot}4 \times 10^{11}$ neutrons. $cm^{-2}.sec^{-1}$ and transferred immediately to a pulse height analyser. Despite the presence of the activity of ruthenium-105, the fast decaying gamma ray of the 42 sec rhodium-104 at 550 keV was easily distinguished in the series of gamma ray spectra obtained at 24 sec intervals. A rhodium content of 31 ppm could be isolated by distillation of the ruthenium tetroxide.

Platinum

Two methods for the determination of rhodium in platinum were proposed by Gauthier.[86] In one procedure rhodium was determined directly without a chemical separation. Samples and standards were subjected simultaneously to a short irradiation and the gamma activity was measured for 10 sec at intervals of 5 sec, thus permitting a determination of purity. In general, long-period activities could be neglected. The precision was about 5%.

The second method involved the production of 36·5 hr rhodium-105 from the reaction $^{104}Ru(n, \gamma)$ $^{105}Ru \xrightarrow{\beta^-} {}^{105}Rh$. The ruthenium tetroxide was removed by distillation and the rhodium-105 was collected by iron hydroxide precipitation. The rhodium was reduced in hydrogen and oxidized to yield rhodium(III) oxide.

A known volume of the dissolved rhodium-105 was added to a hydrochloric acid solution of the platinum and the rhodium was removed by hydrolysis with barium carbonate. The hydrated oxide was washed, dissolved in hydrochloric acid, and rhodium sulphide precipitated by hydrogen sulphide. The rhodium sulphide was ignited to the oxide which was fused selectively with potassium hydrogen sulphate. The melt was dissolved in water, and the solution was filtered to remove platinum which is relatively inert in the fusion, and rhodium was again precipitated as the sulphide. This was washed, ignited, reduced in hydrogen, and weighed, and its activity was counted. A known weight of pure rhodium was similarly treated chemically and a volume of the rhodium-105 tracer, identical to that for the sample, was added. The precision of 4% was about equal to that found for the direct method. Both methods were used for alloys of platinum containing 5, 7 and 11% rhodium.

Meteorites

A variety of analytical methods has been proposed for the determination of noble metals in meteorites. Continued interest in the development of improved methods for meteorites has been encouraged by "the apparent unreliability of previous analytical results for a number of trace elements".[72] Because neutron activation methods lend themselves particularly to the determination of small traces a considerable effort has been made to obtain results by this method. In view of the fact that more accurate results provide some of the incentive for these investigations, it is surprising that little or no effort has been made to confirm the neutron activation results by the application of established methods. As far as the noble metals are concerned, there are spectrophotometric methods available whose sensitivities are sufficient for determinations in many types of meteorites, and some of these applications have been recorded.[73]

With a view to providing more reliable results for the content of rhodium, silver and iridium in chondritic meteorites, Schindewolf and Wahlgren[72] developed a rapid neutron activation method which involved a sodium peroxide fusion, addition of rhodium carrier, treatment with nitrite in a slightly basic medium to hydrolyse the base metals, and a fast filtration by suction. Rhodium in the filtrate was precipitated as the potassium-rhodium-nitrite complex, which was then dissolved in acid, and the metal precipitated by zinc. The chemical yield was determined by weighing after counting. Only 9 min were required for the fusion and chemical separation. The authors state that isotopic exchange between the rhodium of the meteorite and the carrier was confirmed with the 220 d rhodium-102. In the absence of details concerning the zinc precipitation one may expect that the chemical yield obtained by weighing could have a considerable error which is not made evident by a proven purity of isotope.

The standards used by the authors were prepared by adsorption of the rhodium solution on filter paper. Because of the short half-life (4·4 min rhodium-104) the standards and samples were irradiated separately and the activities were monitored by weighed gold foil. It would be expected that the standardization techniques used by the authors would involve the usual errors associated with the matrix differences between sample and standard. Furthermore, it is not made clear how the

use of the 220 d rhodium-102 ensured the isotopic exchange claimed between the carrier rhodium and the activated rhodium in the solution of the carrier.

Counting with the beta proportional counter required about 20–30 min. The degree of reproducibility of the method was determined by the addition of known amounts of the standard to the sample, followed by irradiation, complete separation, and determination. The results indicated an error of 10–15%. However, this technique does not prove the accuracy of the results for the rhodium content of the meteorite.

A general problem associated with the determination of noble metals, particularly the "insoluble noble metals" in iron meteorites is concerned with the potential resistance to dissolution by certain of the noble metal minerals and alloys. Metals such as iridium, osmium, ruthenium and rhodium not infrequently occur in natural formations in a physical condition which is exceptionally resistant to corrosion by normal fusions, acids or even mixed acid treatments. The resistance to mineral acid attack of each of these four metals, in sponge form, with the exception of rhodium in sulphuric acid, is generally recognized. The senior author has in a series of papers dealt with the successful dissolution by mineral acids of iron-nickel-copper alloys containing traces of noble metals. By analogy it would be expected that methods of decomposition by mineral acids or by fusion with sodium peroxide would provide complete dissolution. However, because of the not unlikely possibility that natural occurrences involving prolonged exposure to high temperature may result in alloys with high corrosion resistance, and because an insoluble platinum metals alloy may well contain traces of any one noble metal, all procedures designed to provide a method of determining a noble metal should be concerned with achieving complete dissolution or failing that, at least a qualitative examination of even trace residues.

Iridium

Radiochemical procedures for the determination of iridium were reviewed by Leddicotte[74] in a monograph which included descriptions of the general chemistry of iridium, methods of dissolution, safety practices, general radiochemical information, *etc.* Condensed details were given for 6 procedures.

Noble metals

Kamemoto *et al.*[75] used a non-destructive method for the determination of iridium in amounts of 4·5–90 μg. Fifty-mg samples of platinum, rhodium, palladium and gold and standard iridium were irradiated for 2 hr with a flux of 3×10^{11} neutrons.cm^{-2}.sec^{-1}. Activity measurements were made by comparing the gamma-ray photopeaks of iridium-192 in standards and samples.

Osmium

A non-destructive method of determining iridium in osmium samples containing 9–40% iridium was described by Maxia *et al.*[75a] Mixtures containing powdered metallic osmium and iridium were irradiated for 110 hr with a flux of 10^6 neutrons.cm^{-2}.sec^{-1}. With less than 9% iridium the low activities resulted in doubtful values. Activation at this low flux would permit a wider use of activation methods but it is doubtful whether this particular method is more useful than the classical analytical methods.

Platinum

Methods for determining $1{\cdot}18 \pm 0{\cdot}34 \times 10^{-5}$ mg of iridium in 99·999% pure platinum were described by Airoldi and Germagnoli.[76] From the gamma activity of gold-199 resulting from the beta emission of the 29 min platinum-199, the number of platinum atoms was calculated. From the sum of the closely similar gamma energies of about 300 keV of the 74·4 d iridium-192 the number of iridium atoms was calculated. A second method for iridium involved the prior decay of the platinum activity over a period of 49·4 days.

Javanovitz *et al.*[77] described a neutron activation technique for the determination of traces of iridium in platinum. The work was undertaken to find the practical sensitivity, to evaluate certain chemical separations and the determination of iridium in platinum, and to find the iridium content of certain platinum samples.

The neutron irradiations were made in the Argonne and Oak Ridge reactors. Iridium-192 with a half-life of 74 d was produced from iridium-191 which has a capture cross-section of 1000 barns. A gamma ray scintillation spectrometer was used to avoid minor interferences from other nuclides and to allow an accurate evaluation of the contribution of ^{193}Ir to the platinum counting rates. Counting rates for the sample and standards were measured under the iridium peak at 300 keV. Samples of platinum were purified by fractional crystallization of the hexabromoplatinate. The time required for the transfer the irradiated samples and for the chemical separations allowed the decay of the 19 hr

^{197}Ir and ^{194}Ir. The principal constituents of the radioactivity were then ^{192}Ir, ^{195m}Pt, ^{191}Pt and ^{194}Pt the last three having an overall decay period of 3·8 d. Gold-199 with a half-life of 3·15 d is one of the daughter products and was removed by solvent extraction during the chemical separations. The procedure involved the simultaneous irradiation of pure platinum metal and freshly precipitated hydrated iridium oxide for 12–24 hr. The platinum was dissolved to yield the chloride, and measured amounts of iridium chloride were added. The gold was extracted with ethyl acetate and the iridium was precipitated as the hydrated oxide and separated on filter paper by suction, and then taped to an aluminium disk; the iridium activity induced in the platinum was measured. The platinum filtrate was treated again with the iridium oxide, which was then reprecipitated and counted to ensure complete recovery of active iridium. The final solution of platinum was treated to produce the metal and the residual active iridium was determined. The iridium standards were dissolved and the iridium content determined spectrophotometrically. After activation the weighed iridium sample was dissolved in hot hydrobromic acid and an aliquot was spotted onto a filter paper, dried and counted. Variations in counting rate were determined by the use of equal amounts of the active iridium with different amounts of carrier. Only reasonable statistical fluctuations were observed. Geometric factors were carefully controlled. The results showed that the relative standard deviation for a 0·04 ppm sample was about 10%. The significant errors were ascribed to weighing and variations in chemical treatment and not to the counting rate statistics. The possibility of self-absorption resulting from the high neutron capture cross-section was examined by varying the weights of the standard samples. Self-absorption was not serious provided the iridium content was less than 6 mg. The formation of ^{192}Ir from ^{192}Pt was not significant because the latter is usually present in platinum in low proportions, and high energy neutrons are required for the conversion. The sample was irradiated in a position in the reactor where which the fast neutron flux is negligible in comparison with the thermal neutron flux, but this could limit the sensitivity of the determination.

The method was applied to test the efficiency of the hydrolytic separation of platinum from iridium. The authors commendably note that the "effectiveness of this separation is critically dependent upon the exact conditions and timing with which operations are performed" and that "some practice and experience by the analyst are required before even moderate reproducibility can be achieved." With separations of this nature it is a reasonable conclusion that it is really the analyst's ability that is being tested. The authors found that the 40 mg of iridium carrier initially separated from 100 mg of platinum carried with it 99·10% of the iridium activity. A second and third treatment of the platinum filtrate yielded 0·7% of the activity with the final unrecovered proportion of about 0·2% ascribed to either an inert complex or radiochemical impurities.

It may be suggested that the authors' final reduction of the platinum solution to the metal, which was then examined for iridium activity could be ineffective for the recovery of a trace of iridium. Even magnesium will not necessarily remove iridium quantitatively from a chloroiridate solution. The authors did not specify either the reducing reagent or the procedure used. Furthermore, the results gave only the percentages obtained from the total counts. Any appreciable failure to precipitate iridium in the final platinum filtrate would result in a misinterpretation of the efficiency of the method.

Dopel and Dopel[78] discussed the advantages and disadvantages of neutron activation, spectrographic, and chemical methods of determining traces of iridium in rhodium and platinum. Whereas the established methods have a sensitivity of 10^{-3} to 10^{-2}%, neutron activation techniques could be used for 10^{-5}% iridium or even less. The uncertainties of spectral determinations of concentrations of iridium lower than those accessible to chemical methods did not arise in the neutron activation methods, which required only one iridium standard. Furthermore, the activation methods provide more comprehensive information about the composition of the sample, although they are subject to restrictions associated with favourable conditions for neutron capture, decay periods, and emission energies.

The spectrographic and activation results for the iridium content of rhodium and platinum were in reasonable agreement.

Rhodium

Morris *et al.*[18] gave a neutron activation method for iridium in rhodium without a chemical separation. This was done by a special arrangement which made it possible to plot count rates against pulse height. Because of the large absorption cross-sections for thermal neutrons of both iridium and rhodium and the possible self-shielding differences between samples and standards, the standards were prepared by adding known quantities of ammonium hexachloroidate solution. Samples (0·1 g) and standards were irradiated with a neutron flux of 10^{12} neutrons . cm^{-2} . sec^{-1}. After 8 days the intensities of the photo-peaks 0·316 and 0·47 MeV gamma of iridium-192 were measured in arbitrary units for samples and standards in turn. A check showed that only the gamma rays from ^{192}Ir were being counted. The range of iridium content measured was 3–170 ppm.

The application of gamma–gamma coincidence measurements to the detection and determination of iridium was discussed by Herr and Wolfe.[79] The method was applied to iron oxide, meteorites and purified platinum. The iridium values obtained were closely similar to those obtained by independent methods (which were not specified). For pure platinum the iridium content found was 221 ppm, compared to 217 by the independent method. For platinum of higher purity the values were <44·4 and 42 ppm. The coincidence measurements were made after 14 days decay.

A limited chemical treatment was described. This involved addition of iridium carrier, dissolution in *aqua regia*, conversion into chlorides, addition of gold carrier, and precipitation of the iridium as the hydrated dioxide. In the case of meteorite samples, iridium could be isolated finally as caesium hexachloroiridate. Two single-channel analysers were adjusted to 0·3 MeV for the iridium measurements. The coincidence zero level was 0·03 cpm. Under the conditions used, the sensitivity for iridium was 8×10^{-11} g. The authors state that with irradiation for 2 weeks at 10^{14} neutrons . cm^{-2} . sec^{-1}, the sensitivity could have been increased to 5×10^{-15} g of iridium.

It was noted that valuable samples of meteorites could be analysed non-destructively after a 4-week decay period. Errors arising from self-shielding and depression of the neutron flow were discussed, and specific effects of arsenic and antimony minerals, with the conclusion that antimony introduces significant error.

The authors discussed the general advantages of the gamma–gamma coincidence method, especially its very high selectivity and the elimination of time-consuming chemical treatments. With simple systems there is the advantage of avoiding the destruction of samples.

Undoubtedly, coincidence methods will find extended and useful applications in determinations involving the noble metals, and development of improved counting equipment may confidently be expected.

Palladium

Techniques for the radiometric determination of palladium have been recorded by Spacu and Voicu.[80] The radioactive isotopes palladium-109 and iodine-131 were used to form the insoluble complexes $[PdPy_2I_2]$, $[PdPy_2(SCN)_2]$ or $[PdPy_4][Cr_2O_7]$. Solutions containing 0·5–20 mg of palladium and some pyridine were titrated with a solution of $Na^{131}I$. The activity of the supernatant liquid was monitored to determine the first appearance of activity in the solution. For more than 1 mg of palladium the error varied between 0·34 and 5·5%. A variation of the method involved the simultaneous use of palladium-109 and iodine-131, in which case the end point was located at the minimum of activity in the solution. Precipitation of palladium with thiocyanate or dichromate gave results similar to but less accurate than the iodide results.

A second technique involved extraction of the complexes with chloroform, evaporation of the solvent, and measurement of the activity of the residue. The sensitivity was 0·2 mg of palladium for the iodide precipitate and 0·6 mg for the thiocyanate precipitate.

Iodine-131 indicator was also used by Tölgyessy and Schiller[81] to determine cations which produce an insoluble iodide. The titration beaker was fitted with a Geiger-Mueller counting tube. The titrant for palladium was 0·1*M* potassium iodide containing 1 ml of iodine-131 solution with a specific activity of 0·842 mc/ml.

Procedural details of 17 previously published radiochemical methods for palladium have been recorded, 16 of them involving selective isolation by dimethylglyoxime.[82]

Meteorites

For the determination of palladium in meteorites, Brown and Goldberg[83] irradiated 300–500 mg samples along with standards of palladium dimethylglyoximate. The samples were allowed to cool to remove the 26 min activity of palladium-110. The irradiated samples were dissolved in hydrochloric acid, palladium carrier was added, then ammonia until its concentration reached 0·4*M*, and the glyoximate was precipitated. The precipitate was dissolved in nitric acid, iron carrier was added to scavenge in ammoniacal medium, and was followed by a scavenge with silver iodide. The precipitation steps were repeated and finally the glyoximate was precipitated, weighed and prepared for counting. The irradiated palladium standard was dissolved in nitric acid, treated with carrier and diluted to give a count rate similar to that of the samples.

With such analyses it is unfortunate that few reports suggest any attempt to compare the results with those of established analytical methods. *p*-Nitrosodimethylaniline and other reagents are sensitive enough to be used to determinate less than 1 ppm of palladium in meteorites. Presumably, with the activation methods, it is too often accepted without question that homogeneous distribution of isotopes and carrier is achieved in the sample solution, that energy measurements which confirm the identity of the precipitated metal also indicate the chemical purity of the weighed precipitate. The present authors believe that when neutron activation methods are applied to complex materials such as meteorites, confirmation of these assumptions is required.

Fission product solutions

For the separation of palladium from fission products, Melnick[19] modified Glendenin's procedure,[19] and precipitated the metal first by magnesium and then repeatedly with dimethylglyoxime. Selenium was the only contaminant, appearing as the metal. The precipitate was purified by dissolving it and scavenging with silver chloride and iron(III) hydroxide. The chemical yield was about 75% and duplicate determinations took 5 hr. Techniques were described for counting the activities of palladium-109 and -112 together or separately. Beta counting was started 15 hr after the chemical separation to allow equilibration between 3·2 hr silver-112 and 21 hr palladium-112.

For the separation of palladium from fission products, Alexander *et al.*[84] dissolved the activated uranium foil in *aqua regia* containing palladium carrier. Silver chloride was precipitated with added silver carrier and palladium was extracted as the dimethylglyoximate into chloroform and then back-extracted into concentrated ammonia solution. The solution was scavenged with iron(III) hydroxide, and zinc was added to precipitate metallic palladium. This chemical separation could be done in 3 min. The separation, with some variations, was used to study the short-lived isotopes of palladium-113, -114, and -115 which have half-lives of 1·4 ± 0·1 min, 2·4 ± 0·1 min, and 45 ± 3 sec, respectively.

Platinum

Killick and Morris[85] recorded a procedure for the determination of traces of palladium in platinum. The method was "evolved to provide greater sensitivity than is available with most conventional analytical procedures." The concentration ranges covered were about 0·3–3 ppm. The results given do not indicate an improvement in sensitivity; indeed available spectrophotometric methods will provide greater sensitivity, precision and accuracy. The chemical separation used by the authors involved precipitation by dimethylglyoxime and repeated precipitation as hydrated palladium(II) oxide, removal of silver with a silver carrier, and solvent extraction of gold. The chemical yield was not stated. The authors activated samples and standard with a thermal neutron flux of 10^{12} neutrons. cm^{-2}. sec^{-1} and the activity of 13·5 hr palladium-109 was measured. Corrections were made for chemical yield, paralysis and background. Similar weights of palladium dimethylglyoximate were counted, and self-shielding differences between samples and standards were avoided by adding known small quantities of standard palladium solutions. Decay characteristics of the precipitate were measured to ensure that only the activities of palladium-109 were measured. The time needed for chemical separation ensured the removal of the relatively short lived palladium-111.

Platinum

Aluminium

A comparison of chemical and neutron activation methods of determining platinum and chlorine in alumina-base platinum-chlorine type re-forming catalysts was made by Guinn and Wagner.[86] Unfortunately the chemical method was not specified, which eliminates much of the usefulness of the comparison. The gamma spectrum of 0·72–0·79 MeV of the 30 min platinum-199 was used for the determinations which involved no chemical operations. For determinations of amounts of platinum of the order used for spectrophotometric methods the authors preferred the activation method because of the relatively short period required for a determination. The values reported for platinum indicated good precision for both methods but the discrepancies between the two methods were significant. Additional comparisons of this type made with clearly delineated and acceptable techniques may be hoped for.

MULTI-COMPONENT NOBLE METAL SYSTEMS

Rocks

Gold and palladium. Neutron activation techniques were used by Vincent and Smales[30] to determine palladium and gold in igneous rocks. These authors deal briefly with the deficiencies of some of the recorded earlier methods of assay. It may be noted here that the methods chosen by the authors for comparison are by no means representative of the best classical methods, and that the comment that "the possibility of serious losses of trace amounts of precious metals during the fire assay seems largely to have been overlooked, or at best seriously under-estimated" is incorrect and so is the inference that results have been available to indicate the failure of classical methods in the determination of trace amounts of the noble metals in ores. To the best of the present authors' knowledge no results have been recorded to indicate either the success or failure of recovery of microgram amounts of noble metals from ores. Here distinction must be made between loss of a metal present as a trace and trace losses associated with the recovery of larger amounts of metal.

It is further stated[30] that "since most of the available data on the palladium and gold contents of rocks have been obtained by some kind of fire assay some doubt must always remain as to their

accuracy, and the adoption of a radioactivation method, eliminating all possibility both of losses of palladium and gold from the samples and of reagent contamination, seemed desirable." Presumably, the authors feel that by avoiding losses one may remove doubt concerning accuracy and that neutron activation techniques will accomplish this very desirable situation. This has not been accomplished during the decade following the report, and a neutron activation method for ore samples which, in general, eliminates doubt concerning the accuracy of palladium and gold determinations is not likely to be developed within the predictable future, if at all.

Vincent and Smales irradiated 100–200 mg of rock powder and standards of palladium and gold foil for about 12 hr. The irradiated rock powder was sintered with sodium peroxide, the moistened sintered cake was transferred to a small beaker and carrier gold and palladium were added as foil. The mixture was treated with *aqua regia*, the solution evaporated, and the hydrochloric acid extract was centrifuged to remove the silica. Hold-back carriers of sodium nitrate, potassium chloride, copper(II) chloride, and nitrates of cobalt, zinc and manganese were added to the centrifuged liquid; palladium and gold were precipitated by magnesium, the precipitate was redissolved in *aqua regia*, and gold was finally extracted from the chloride solution with ehtyl acetate. The organic layer was evaporated, and after a purification process, including the use of hold-back carriers, the hydroquinone-gold precipitate was purified and weighed to establish the chemical yield, and then the activity of the 2·7 d gold-198 was counted.

The irradiated gold standard was allowed to stand for about 1 week, then dissolved, and suitable aliquots were treated with carrier gold foil and the gold was isolated and treated as described above for the irradiated ore.

To isolate palladium the aqueous extract from the gold separation was treated to precipitate palladium dimethylglyoximate; this was then dissolved, and the resulting solution was treated with solutions of iron(III) chloride, manganese(II) chloride, bromine water and ammonia. The filtrate from the hydrated oxides was treated with hold-back carriers, and then subjected to a silver iodide precipitation and then a reprecipitation of palladium dimethylglyoximate. After repeated reprecipitations, the precipitate was dried and weighed, and its activity was counted. The irradiated palladium standard was treated with carrier, the dimethylglyoximate precipitated and weighed, and the activity of the 13·3 hr palladium-108 counted. The chemical yield for gold was about 80% and for palladium 50–60%.

On the basis of a counting rate of 10 cpm above the background, the use of a 100 mg sample and a 50% chemical yield, the authors accepted a sensitivity limit of 0·01 ppm of palladium. For gold with a 70% chemical yield the limit was 0·002 ppm. In both instances with more favourable irradiating conditions, *etc.*, the limits may be reduced to 0·005 ppm of palladium and 0·0005 ppm of gold. Such techniques as scavenging with highly adsorbent hydrated oxides, *etc.*, should be examined experimentally to determine the effect, if any, on isotopic homogeneity. The statement that "the active atoms of the analysis element contributed by the rock interchange freely with the inactive atoms from the carrier, having identical chemical but different nuclear properties" presupposes that the chemical properties of the dissolved metal constituents are indeed identical, and this also should be checked.

Ores

Neutron activation methods for the determination of noble metals in ores have been reported. As stated in the introduction, if the irradiated ore is not completely dissolved, the proposed procedures can be accepted only as methods of determining noble metals in liquid extracts; they cannot be properly described as methods of determination in ores.

Palladium and platinum. Morris, Hill and Smith[87] used neutron activation methods to determine palladium and platinum in pentlandite, pyrrhotite and chalcopyrite concentrates obtained from Sudbury ores by flotation and magnetic separation. Finely ground samples (0·5 g), some with addition of aliquots of standard palladium and platinum solution, were irradiated for 1 week in a nuclear reactor flux of $1{\cdot}2 \times 10^{12}$ neutrons . cm^{-2} . sec^{-1}. The irradiated materials were cooled for about 5 hr, treated with palladium and platinum carriers, and then dissolved in nitric and hydrobromic acids. It may be assumed that at least a small insoluble residue remained. The acid extract was evaporated and the residue treated with hydrobromic acid, and the metals were precipitated by magnesium. The supernatant liquid was discarded and the precipitate was dissolved in nitric and hydrochloric acids, gold carrier was added, and the gold was extracted with ethyl acetate. The aqueous phase was treated to precipitate palladium dimethylglyoximate which was then purified by dissolution in hydrochloric acid and extraction with chloroform. The solvent was evaporated and the palladium was converted into the chloride. Silver carrier was added and the silver chloride was removed. Finally palladium dimethylglyoximate was precipitated and weighed, and the beta activity of palladium-109 was counted. The supernatant liquid from the palladium dimethylglyoximate was treated with mercury(I) chloride to precipitate platinum which was then dissolved and finally precipitated as ammonium hexachloroplatinate. This precipitate was dissolved, the solution was treated

with tin(II) chloride, and the coloured constituent was extracted with ethyl acetate. The solvent was evaporated and the residue was treated with sodium nitrite to remove base metals, and the platinum was finally precipitated by mercury(I) chloride; the beta activity for platinum-197 was counted. The chemical yield for platinum was determined by measuring the absorbance of the chloro-complex. All counting rates were corrected for paralysis, background, decay, and chemical yield, which was about 80% for palladium and 50–60% for platinum.

The results obtained showed values for pentlandite which are well within the range of spectrophotometric determinations, and these methods could have been used to provide direct comparisons of results from activation and standard methods.

Ruthenium and osmium. Traces of ruthenium, osmium and uranium in materials such as chondrites, achondrites, tektites, trolite, and terrestrial rocks, *etc.*, were determined by Bate and Huizenga[88] by neutron activation techniques. After irradiation the samples were fused in sodium peroxide with the carriers $[Ru_2(OH)_2Cl_4 \cdot 7NH_3 \cdot 3H_2O]$ and K_2OsCl_6. The caustic solution was treated with ethanol to precipitate hydrated ruthenium oxide and the filtrate was treated with hydrogen sulphide to precipitate "osmium oxide". The ruthenium oxide was distilled from a sodium bismuthate suspension and collected in sodium hydroxide. Subsequent purification procedures included solvent extraction of the octavalent oxide by carbon tetrachloride, back-extraction with sodium hydroxide, precipitation by ethanol, scavenging and precipitation of gold by hydrazine hydrochloride, further scavenging with lead iodide and cadmium sulphide, and finally precipitation of ruthenium oxide and treatment of the supernatant liquid with hydrogen sulphide to recover the residual ruthenium. The combined ruthenium precipitates were again subjected to a bismuthate distillation and treatment with ethanol, and finally the ruthenium was precipitated as caesium hexachlororuthenate which was mounted on a weighed filter paper for counting.

The initial osmium precipitate was treated by distillation, solvent extraction, scavenging and precipitation as for ruthenium. The final precipitate of caesium hexachloro-osmate was mounted as for ruthenium and counted.

Recovery tests were made with known amounts of osmium and ruthenium on strips of glass fibre filter paper, buried in a matrix of powdered dunite. The mixtures were irradiated for 24 hr at a flux of 6×10^{12} neutrons . cm^{-2} . sec^{-1}. The extent of recovery was obtained by comparing the count rates of the sample, corrected for chemical yield, with those of the flux monitors simultaneously irradiated. The energy spectra for samples and flux monitors were identical, and free from extraneous activities. The activities were identified by their half-lives.

The work was carefully done, but the analytical approach involved an unduly lengthy and unnecessarily cumbersome series of techniques. The problems presented by the explanations for the good recoveries of osmium relative to those of ruthenium could be solved very readily by simple experiments, but the authors had, as is also found in the early analytical literature, some degree of misconception concerning the ease of oxidation of ruthenium to form the volatile octavalent oxide.

Meteorites

Gold and palladium. For the determination of gold and palladium in iron meteorites, Goldberg, Uchiyama and Brown[89] used the neutron activation and radiochemical methods described by Brown and Goldberg.[83] For palladium, precision at the 1 ppm level was about 10% and for gold 10–15%. A correction factor of 25% was applied to allow for the self-shadowing effect of gold in the samples.

Iridium, gold and platinum. Rushbrook and Ehmann[3] used activation methods for the determination of iridium in stone meteorites. The meteorite samples and the aluminium disk flux monitors containing an evaporated residue of standard iridium solution were irradiated for 4–6 hr at a flux of about 2×10^{12} neutrons. cm^{-2} . sec^{-1}. The chemical procedure involved addition of the irradiated sample to the iridium carrier solution, treatments with hydrochloric, nitric, hydrofluoric and sulphuric acids and *aqua regia* to dissolve all but a small residue which presumably was discarded. Iridium was taken out on an anion-exchanger, Dowex 1-X8, pretreated with cerium(IV) solution. The column was washed free from iron by 0·8*M* hydrochloric acid, and the iridium on the column was reduced to the tervalent form by hydroxylamine hydrochloride (and thereby partially eluted), and then eluted with 8·0*M* hydrochloric acid. (This process for the separation of iridium should receive a quantitative analytical examination.) The iridium eluate was treated first with peroxide and then with zinc, the excess of which was removed by treatment with acid. The iridium precipitate was separated, purified by treatment with *aqua regia*, filtered, washed with glacial acetic acid and water, dried, and weighed. The gamma-ray spectrum of the precipitate indicated the absence of impurities. The chemical yield ranged from 70 to 95%. Counts were made at the 0·316 MeV gamma-ray peak of the 74·7 d iridium-192. Positive identification was made by means of the iridium-192 gamma-ray peak at 0·47 MeV. No iridium activity was detected in the aluminium discs used for blanks.

These researches were extended by Baedecker and Ehmann[90] to include determinations of gold,

platinum, and iridium in meteoritic and terrestrial materials. The three metals were sometimes determined simultaneously in a single sample. The techniques used for sample preparation, dissolution, monitoring, irradiation, and iridium separation were previously discussed.[3]

When the three metals were determined simultaneously, they were adsorbed selectively on Dowex 2-X8 anion-exchanger, then iridium was eluted first with hydroxylamine and hydrochloric acid as previously described,[3] then gold with a solution of thiourea in dilute hydrochloric acid. The gold eluate was treated with ammonia, the gold sulphide produced was dissolved, and the gold extracted by ethyl acetate and finally precipitated by hydroquinone, purified, dried and weighed, and its activity was counted at the 0·411 MeV peak of gold-198. Platinum was not isolated chemically but was determined indirectly by counting at the 0·158 MeV peak of the 3·14 d gold-199 produced indirectly from platinum-198. Problems arose from the simultaneous production of gold-199 through double neutron capture by gold-197. Methods of avoiding the error were discussed. The preferred method involved the subtraction of the gold-198 spectrum from a gold flux monitor (which automatically included the gold-199 activity caused by the double neutron capture by gold-197, and the gold-198 Compton distribution). The total error for platinum was about ±20%. The error for gold and iridium was ±8–10%. For the latter element the 0·31, 0·47 and 0·61 MeV gamma-ray peaks of 74·37 d iridium-192 were used for counting.

Platinum, iridium and palladium. A neutron activation method for the determination of platinum, iridium and palladium in meteorites was recorded by Hamaguchi, Nakai and Kamemot.[91] The method uses a cation-exchange separation previously recorded by Stevenson *et al.*[92] and applied by Karttunen and Evans[93] to the separation of rhodium from palladium.

Solutions of the irradiated meteorite were treated with noble metal carriers and then with magnesium. The precipitate was fused with sodium peroxide and hydroxide, the cooled melt was leached with water and the residue was dissolved in hydrochloric acid. The metal constituents were oxidized with chlorine, and then platinum and iridium were precipitated as the ammonium hexachloro-salts. Palladium in the filtrate was purified by reprecipitation with dimethylglyoxime after scavenging with iron hydroxide. The chloro-salts were dissolved and treated with perchloric and nitric acids, the perchlorates were passed through a cation-exchanger, and the metals were eluted selectively. Platinum was purified by solvent extraction with ethyl acetate to remove gold and with ethyl acetate and tin(II) chloride to separate the platinum, which was finally precipitated by magnesium. Palladium, the second to be eluted from the cation-exchanger was purified by treatment with dimethylglyoxime alternating with scavenging with iron hydroxide.

Iridium in the third fraction of eluate was precipitated by magnesium. Initially the meteorites were irradiated for 2–3 d (5 hr/day) with a flux of 10^{11} neutrons . cm^{-2} . sec^{-1}. Standards were prepared by adding the noble metals to a mixture which simulated the composition of a meteorite.

ALLOYS

Gold and palladium in aluminium

For the determination of impurities in very high purity aluminium including gold and palladium, Gaittet[94] described a procedure for the separation of the two metals from tellurium by extracting gold bromide with ether and precipitating palladium with dimethylglyoxime.

Gold and platinum metals in silver

Zvyangintsev and Kulak[95] determined gold and platinum metals in refined silver by neutron activation. The isotopes used were gold-197, platinum-192 and -196, palladium-102 and -108, iridium-191 and -193. The interference from palladium-109 produced from silver was avoided by the use of fluxes of 5×10^{9}–10^{10} and 10^{11}–5×10^{13} neutrons . cm^{-2} . sec^{-1}. The activity of the isolated precipitates was compared with the activity of standards, and corrections made for chemical yield of the carrier and for self-absorption in the sample. The silver samples were irradiated in the form of thin shavings to reduce self-absorption. Irradiation of samples in the form of blocks was considered to be unsatisfactory. After irradiation, the samples and standards were dissolved in nitric acid, and carriers for each of the constituents to be determined were added in amounts of 15–20 mg. Silver was removed as the chloride, gold and copper by nitrite, palladium by dimethylglyoxime, iridium by hydrolysis to the hydrated dioxide and platinum by mercury(I) chloride. Gold was separated from copper by solvent extraction and then precipitated by sulphur dioxide. The chemical yield was determined gravimetrically. The authors sought to achieve radioactive purity by dissolving each precipitate, adding appropriate carriers, and reprecipitating. Traces of active silver were removed similarly by adding silver to the initial silver chloride filtrate and filtering off the silver chloride. Here, it may be noted that a silver chloride precipitate preferentially adsorbs palladium from solution, and because the mechanism of this phenomenon has not been established, the effect, if any, of this adsorption upon isotopic homogeneity ought to be investigated.

There is also the question of incomplete dissolution of iridium/silver alloys. To the best of the present authors' knowledge no results have been recorded to indicate that even traces of iridium can be completely dissolved by treatment of a cupelled silver alloy with nitric acid solutions. Furthermore, the technique used by the authors to determine radioactive purity may not necessarily indicate chemical purity. In any case, the authors record a precision for the method of only ±5–20%. It is noted that no comparative results were given for the chemical determination of iridium, though they were included for gold, platinum and palladium.

Gold and platinum in silicon

For the determination of 29 elements, including gold and platinum, in ultra-pure silicon Thompson *et al.*[25] applied a modification of the classical separations, and made beta and gamma activity measurements. Gold was separated by formation of gold and arsenic sulphides, followed by treatment with hydrochloric, nitric and perchloric acids, addition of potassium iodide and solvent extraction with carbon tetrachloride. Chromium(II) chloride was used to precipitate the gold. Platinum was isolated as the sulphide together with cadmium, molybdenum, mercury and tin, and finally precipitated as metal by chromium(II) chloride. The concentrations of gold were as small as 5×10^{-5} ppm, and of platinum, 9×10^{-4} ppm.

Osmium and iridium in platinum and palladium

A neutron-activation method for the determination of submicro amounts of osmium and iridium in platinum and palladium was recorded by Morris and Killick.[96] The samples were activated for 1 week with fluxes of 10^{12} neutrons.cm^{-2}.sec^{-1} for palladium and 9×10^{11} neutrons.cm^{-2}.sec^{-1} for platinum. Measured amounts of standard solutions of ammonium hexachloro-osmate and hexachloroiridate were added to 0·1 g each of platinum and palladium powder. Activity measurements were made on 30·6 hr osmium-193, 16 d osmium-191, 19 hr iridium-194 and 74 d iridium-192. All activities for osmium were measured with a Geiger-Mueller counter and for iridium with a gamma-scintillation counter, and corrected for paralysis, background and chemical yield. No figures for the chemical yield were reported. The radiochemical purity of the separated osmium and iridium was confirmed by decay measurements. The possibility of errors arising from certain conflicting nuclear processes was examined experimentally. The activating flux used for palladium was applied also to platinum in which case the corresponding flux of fast neutrons was $1{\cdot}6 \times 10^{11}$ neutrons.cm^{-2}.sec^{-1} as compared to the fast neutron flux of 5×10^{8} used initially for the platinum activation. The average result for osmium was 0·36 ppm as compared to 0·33 ppm obtained with the flux of 9×10^{11} neutrons.cm^{-2}.sec^{-1}. In the case of iridium the respective values were 0·66 ppm and 0·50 ppm. Errors from the conflicting nuclear processes could therefore be ignored. Interference from other possible nuclear reactions was shown by calculation to be negligible. The authors reported values for osmium in the range 0·08–1·06 ppm, and for iridium, 0·097–11·1 ppm. The osmium solutions were standardised by evaporation and reduction of the residue in hydrogen to produce osmium as the weighing form; the iridium solutions were standardised by hydrolytic precipitation.

After irradiation the material was dissolved in hydrochloric acid and osmium and iridium carriers were added. Osmium tetroxide was distilled from nitric acid solution and collected in a solution of sodium hydroxide and methanol. The osmium was precipitated hydrolytically, and the oxide was converted into the metal by reduction with hydrogen, and the metal was weighed to establish the chemical yield. The pot liquid was treated to remove platinum, rhodium, *etc.*, selectively by mercury(I) chloride and sodium bromide, then iridium in the filtrate was precipitated as the hydrated oxide, which was then dissolved in hydrochloric acid and fumed with perchloric acid, and the iridium was extracted by pyridine from sodium hydroxide solution. The pyridine extract was then treated to produce finally hydrated iridium(IV) oxide; the oxide was ignited to yield the metal, the activity of which was counted.

It is unfortunate that the authors did not give the chemical yield. The procedure for the determination of iridium offers new features and if analytically effective could provide useful alternative methods for iridium after removal of osmium.

Ruthenium, palladium and platinum in beryllium

Zarmyatnina *et al.*[97] mixed standard samples of palladium chloride, chloroplatinic acid and ruthenium nitrosopentachloride and irradiated them in a uniform thermal neutron flux. The samples and standards together with carriers were dissolved in hydrochloric acid and hydrogen peroxide. Ruthenium was isolated by distillation into sodium hydroxide solution, then precipitated by ethanol. Palladium and platinum were precipitated as sulphides. Palladium was separated by precipitation as the dimethylglyoximate, selective extraction with butyl phosphate, and precipitation again as

first the glyoximate and finally the sulphide. Platinum was separated by extraction with butyl phosphate and benzene and finally by precipitation of the sulphide. The weighing forms were ruthenium(IV) oxide and platinum and palladium metals. Activities were measured for ruthenium-106, palladium-109 and platinum-197. The lanthanides were also determined.

Rhodium, iridium and gold

The increasing interest in the analytical use of short-lived isotopes is made evident by a variety of publications. Anders[48] used isotopes with 5–24 sec half-lives for the determination of 18 elements including rhodium, iridium and gold. Irradiations were made at a flux of 2×10^8 neutrons.cm^{-2}.sec^{-1}. The activation analysis required less than ½ hr and for about 15 mg of gold the relative deviation was about 4%. By the subtraction of the spectrum taken 32 sec after irradiation from the spectrum taken 2 sec after irradiation, most of the longer-lived contributions were suppressed. The results were interpreted by comparing the number of counts in the photopeak ranges of the difference spectra for both samples and standards. Cumulative spectra were collected with a "rabbit" to serve as a background correction.

Iridium, platinum and gold

In a study of the radiation characteristics of the active isotopes of iridium, platinum and gold, Wilkinson[98] used conventional methods of dissolution and chemical separation. For the dissolution of iridium he used the bomb method of Wichers, Schlect and Gordon,[99] and after removing osmium, gold and platinum, precipitated iridium as the hydrated dioxide. For large amounts of iridium the ammonium chloride method was applied. Osmium was removed by distillation of the tetroxide from nitric acid and finally precipitated by magnesium. Gold was then removed by solvent extraction and precipitated by sulphur dioxide; this was followed by the extraction of platinum as the tin(II) complex and precipitation of the metal by magnesium. The final precipitates were washed with acetone and mounted as the metal for counting, or were dissolved and the resulting solutions were evaporated to yield residues which were used for counting.

Ruthenium and palladium in fission products

In a study of the fission of thorium with alpha particles Newton[100] isolated ruthenium from the products by distillation with perchloric acid and sodium bismuthate, collected the tetroxide in a solution of sodium hydroxide, and precipitated the hydrated oxide with ethanol and finally the metal with magnesium. He removed palladium with dimethylglyoxime, dissolved the glyoximate in nitric acid, made the solution ammoniacal, and precipitated silver iodide. The glyoximate was again separated from the solution, and mounted for counting.

DISCUSSION

Considered in retrospect, the research reports reviewed here suggest a few comments based on some 30 years of experience in the field of noble metal research.

Those analytical chemists who have struggled to establish experimentally the relative efficiency and the applicability of newly proposed techniques must find astonishing the apparent confidence with which the efficiency of analytical activation methods for such complex materials as ores, alloys, *etc.*, are accepted by their authors. The almost constant failure to deal adequately with the problem of efficiency relative to proved methods is especially disappointing when there frequently exist other techniques for determining trace constituents, which could be used for comparison. The need for a comparison of accuracy is sometimes met by casual references to adverse characteristics of other published chemical and physical methods, with the intention of placing the proposed method in a favourable perspective. This approach is not, of course, a characteristic only of activation methods; too often it has presented a misleading interpretation of the researches to which reference is made. Furthermore, such unfavourable comparisons, without the backing of the unmistakable mark of experience, serve only to initiate lack of confidence in the reports.

In many of the earlier activation methods the more unacceptable separatory

procedures and reagents seem often to have been used. This deficiency is particularly evident in the analytical methods for iridium and ruthenium. On the other hand, in the more recent reports of activation methods, a number of new reagents for both the separation and determination of noble metals has been proposed and results for known separatory processes have been provided which indicate the advisability of re-examining some of the classical analytical methods. A case in point is the report[69] that iridium may be volatilized from perchloric acid solutions.

It is emphasized again that for a wide variety of purposes, involving the detection and determination of submicrogram traces, the activation techniques now available will meet a fast growing need that, in general, is not met by any other existing analytical technique. Indeed, Herr and Woolfe[79] have proposed that terms indicating a new dimension of purity will now be required and it is suggested that "nuclear pure" must be added to distinguish from "chemically pure" and "spectrally pure." It is to be hoped that each of these terms will be more clearly defined.

Résumé—On passe en revue de façon critique, jusqu'en décembre 1965, les méthodes par activation de neutrons pour les sept métaux nobles. Les méthodes traitent de la détermination d'impuretés à l'état de traces dans chaque métal noble ainsi que de la détermination de traces de métaux nobles dans des milieux tels que substances organiques, produits de fission et autres solutions, minerais, alliages, minéraux, silice et métaux de base. On met en évidence la nécessité de preuves confirmatoires dans le cas de matériaux complexes comme les minerais.

Zusammenfassung—Es wird eine kritische Übersicht über Neutronenaktivierungsmethoden zur Bestimmung der sieben Edelmetalle bis Dezember 1965 gegeben. Die Methoden befassen sich mit der Bestimmung von Spurenverunreinigungen in jedem Edelmetall sowie mit Edelmetallspuren in Medien wie organischem Material, Lösungen von Spaltprodukten und anderen Lösungen, Erzen, Legierungen, Mineralien, Kieselerde und unedlen Metallen. Es wird Nachdruck auf die Feststellung gelegt, daß bei so kompliziert zusammengesetzten Substanzen wie Erzen zusätzliche Informationen notwendig sind.

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A NEW OXIDIMETRIC REAGENT: POTASSIUM DICHROMATE IN A STRONG PHOSPHORIC ACID MEDIUM—VII*

PHOTOMETRIC TITRATION OF VANADIUM(IV) AND OF CERIUM(III) ALONE AND IN MIXTURES WITH IRON(II)

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Summary—Vanadium(IV) can be accurately titrated with potassium dichromate in media containing phosphoric acid of 3–12*M* concentration: the change in absorption of vanadium(IV) is followed in the region 660 mμ using a red filter. It is more convenient to carry out the titration in 3*M* phosphoric acid because at higher concentrations chloride, nitrate, cerium(III) and manganese(II) may interfere. Photometric titration is more convenient than potentiometric because the former can be made in a 3*M* phosphoric acid medium, whereas the latter is possible only in 12*M* phosphoric acid. The simultaneous differential photometric titration of iron(II) and vanadium(IV) is also possible. Conditions have been found for the photometric titration of cerium(III) and of cerium(III) plus iron(II). The titration is carried out (at 450 mμ or with a blue filter) in about 10.5*M* phosphoric acid. Application of the method to a cerium mineral is considered.

GODDU AND HUME[1] titrated vanadium(IV) with potassium permanganate photometrically at 525 mμ. The relative error was 0·5–1·0%. Chromium(III) interfered when the ratio chromium(III): vanadium(IV) exceeded 10; tungsten(VI) also interfered. Gopala Rao and Kanta Rao[2,3] titrated vanadium(IV) and cerium(III) potentiometrically with potassium dichromate in phosphoric acid medium. We have now investigated the same titrations with a photometric end-point.

EXPERIMENTAL

Reagents

Cerium(IV) solution, 0·1*M*. Prepared in 1*M* sulphuric acid from *Pro Analysi* cerium(IV) sulphate and standardised as previously described.[3]

Cerium(III) solution, 0·1*M*. Prepared in 1*M* sulphuric acid and standardised.[3]

Vanadium(IV) solution, 0·1*M*. Prepared in 0·5*M* sulphuric acid and standardised as described previously.[3]

Vanadium(V) solution, 0·1*M*. Prepared from analytical reagent grade ammonium vanadate (B.D.H. Ltd., England), by heating with a slight excess of analytical reagent grade sodium carbonate until ammonia is completely driven off, and then dissolving the product in water. The solution was standardised against a standard solution of iron(II) sulphate with barium diphenylamine sulphonate as indicator.

Potassium dichromate solutions. Prepared from *Pro Analysi* grade potassium dichromate (E. Merck, Germany) in the required concentrations of phosphoric acid.

Syrupy phosphoric acid. Pro Analysi grade phosphoric (E. Merck, Germany) was purified as previously described.[4] For determination of the absorption spectrum of cerium(IV) and chromium(VI) neither syrupy phosphoric acid of *Pro Analysi* grade nor analytical reagent grade acid was satisfactory because of the presence of traces of reducing impurities which react rapidly with cerium(IV) and chromium(VI).

Absorption spectra

Solutions of vanadium(IV), vanadium(V), cerium(IV) and potassium dichromate in various concentrations of phosphoric acid were prepared, and their absorption spectra measured. A Hilger Uvispek spectrophotometer with 1-cm glass cells was used. The absorption spectra are shown in Figs.1–4. Cerium(III) in phosphoric acid (12*M*) shows no absorption over the range of wavelengths

* Part VI: *Talanta*, 1966, **13**, 1335.

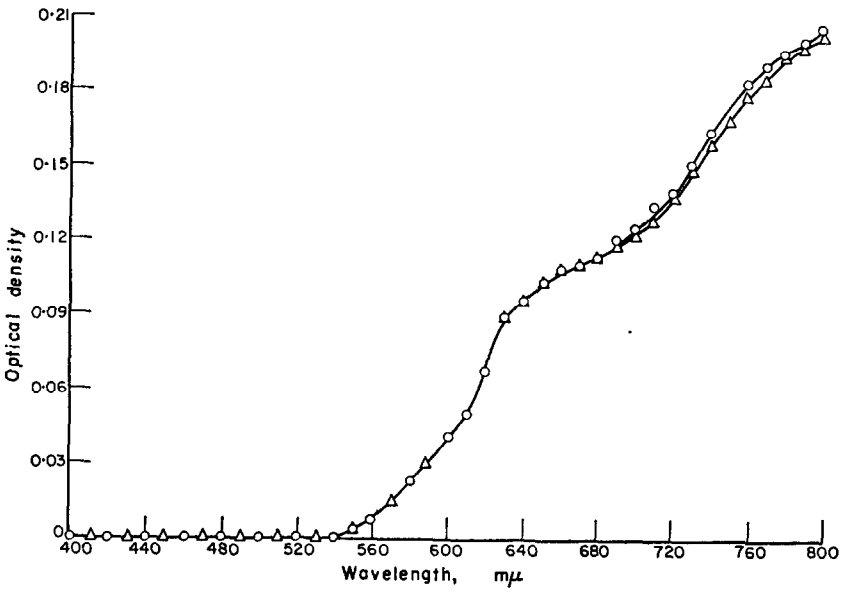

FIG. 1.—Effect of phosphoric acid concentration on the absorption spectrum of 0·01*M* vanadium(IV):
⊙—⊙ 1·5*M* H_3PO_4,
△—△ 3·0*M* H_3PO_4.

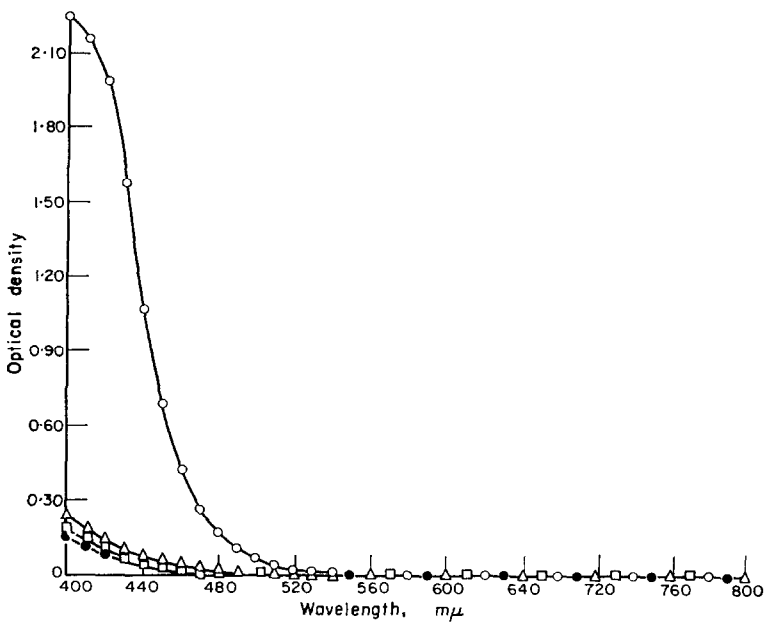

FIG. 2.—Effect of phosphoric acid concentration on the absorption spectrum of 0·01*M* vanadium(V):
⊙—⊙ 10·5*M* H_3PO_4,
△—△ 4·5*M* H_3PO_4,
⊡—⊡ 3·0*M* H_3PO_4,
●—● 1·5*M* H_3PO_4.

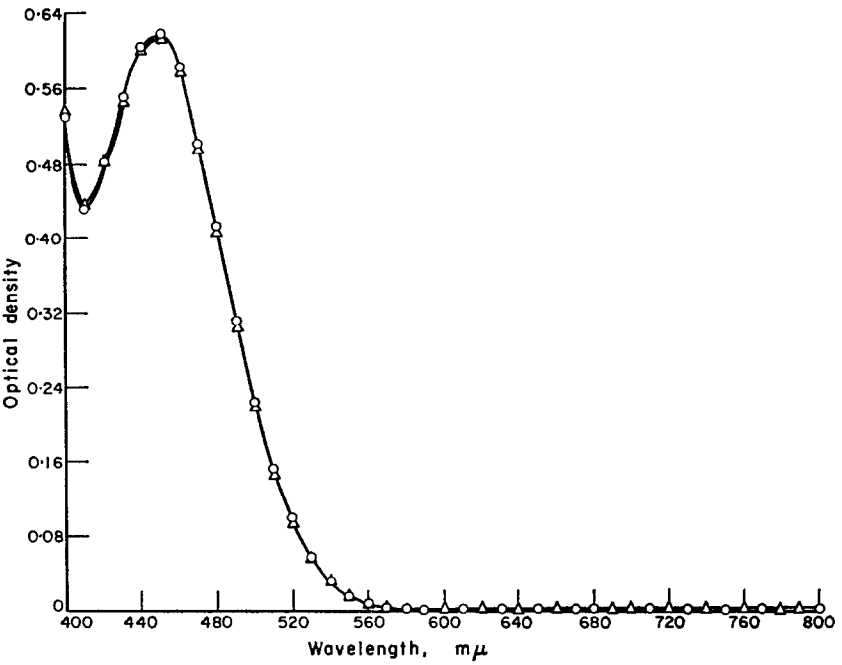

FIG. 3.—Effect of phosphoric acid concentration on the absorption spectrum of 0·0033*M* chromium(VI)
○—⊙ 4·5*M* H_3PO_4,
△—△ 12·0*M* H_3PO_4.

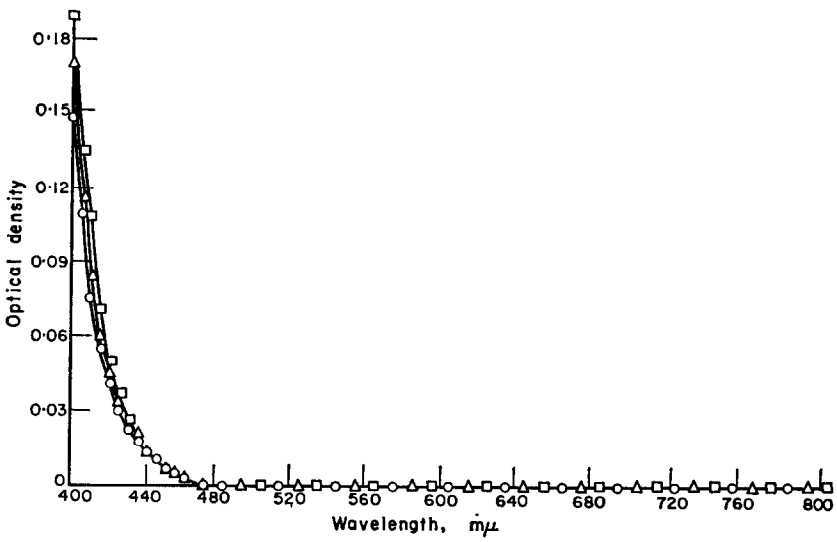

FIG. 4.—Effect of phosphoric acid concentration on the absorption spectrum of 0·01*M* cerium(IV):
⊡—⊡ 9·0*M* H_3PO_4,
△—△ 10·5*M* H_3PO_4,
○—⊙ 12·0*M* H_3PO_4.

covered. From these absorption spectra and those already published for vanadium(IV)[5] and chromium(III),[4] the best wavelengths for the spectrophotometric titration of vanadium(IV) and cerium(III) can be selected. For the titration of iron(II) and vanadium(IV) in the same solution, or iron(II) and cerium(III), advantage can be taken of the large difference in the molar absorptivity between chromium(III) and vanadium(IV) at 660 mμ and between chromium(III) and chromium(VI) at 450 mμ, to yield separate end-points for the iron(II) oxidation and the oxidation of the other reductant present.

Rate of reaction

To find the concentration of phosphoric acid at which a rapid oxidation of vanadium(IV) or cerium(III) occurs, we measured at different time intervals the absorbance of a mixture of vanadium(IV) or cerium(III) with an equivalent amount of potassium dichromate at a suitable wavelength. The results are given in Table I. At 660 mμ the initial absorbance is due to vanadium(IV) and the final absorbance to chromium(III). At 450 mμ the absorbance of chromium(VI) decreases as reaction proceeds.

TABLE I.—EFFECT OF PHOSPHORIC ACID CONCENTRATION ON TIME NEEDED TO COMPLETE REACTION BETWEEN CHROMIUM(VI) AND VANADIUM(IV) OR CERIUM(III)

	Time needed, *min*								
Phosphoric acid concentration, *M*	0·75	1·5	3·0	4·5	6·0	7·5	9·0	10·5	12·0
Vanadium(IV)	7	3	2	2	1	1	1	1	1
Cerium(III)	—	—	—	—	—	40	10	1	1

If the phosphoric acid concentration is higher than 7*M*, then ions such as manganese(II), cerium(III) and nitrate interfere with the vanadium titration. For this reason 3*M* phosphoric acid is used as the titration medium for vanadium(IV) and the spectrophotometer readings are taken 3 min after each addition of the titrant.

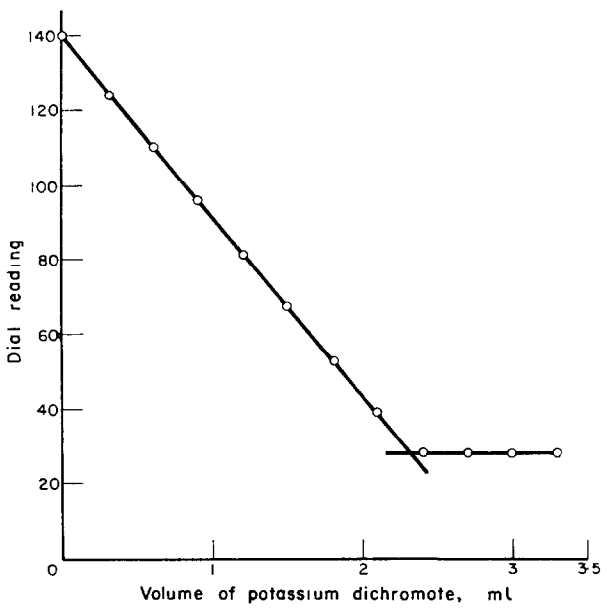

FIG. 5.—Photometric titration of vanadium(IV) (16·44 mg) with 0·2*N* potassium dichromate in a 3*M* phosphoric acid medium.

Procedure for vanadium

Take 2–10 ml of vanadium(IV) solution (containing 10–50 mg of vanadium) in an optical cell (a convenient size is 2 × 4 × 8 cm), add 10 ml of syrupy phosphoric acid, and dilute to 40 ml with water. Arrange an inlet tube so that it is immersed in the solution at one corner of the cell, out of the light-path. Pass carbon dioxide through the solution to mix it and maintain an inert atmosphere above it, and stop the passage of gas before taking a reading of the absorbance. Titrate photometrically at 660 mμ (or with a red filter), adding 0·2*N* potassium dichromate from a microburette, and taking readings 3 min after each addition. Plot absorbance (corrected for dilution) against volume of titrant added. The absorbance decreases as vanadium(IV) is oxidised, and becomes constant at the end-point. A typical curve is shown in Fig. 5, and typical results in Table II. The maximum relative error is 0·7%.

TABLE II.—PHOTOMETRIC TITRATION OF VANADIUM(IV) WITH POTASSIUM DICHROMATE IN A 3*M* PHOSPHORIC ACID MEDIUM

Vanadium(IV), *mg*	
Taken	Found
12·35	12·28
16·44	16·50
23·01	23·13
25·61	25·48
29·13	29·32
35·76	36·01
43·30	43·40
50·71	50·94

Interferences

Iron(II), arsenic(III), antimony(III), uranium(IV) and molybdenum(V) are also oxidised by potassium dichromate under the conditions proposed for the photometric titration of vanadium(IV). However, a separate equivalence point can be obtained from the photometric titration curve when iron(II) is present with vanadium(IV) (see later). Large amounts of chloride and nitrate do not interfere. Iron(III), cerium(III), manganese(II), cobalt(II), nickel(II), molybdenum(VI), uranium(VI), chromium(III) and zinc(II) do not interfere (see Table III). Tungsten(VI) interferes under the conditions proposed for the photometric titration of vanadium(IV), which forms a coloured solution with tungsten(VI). This interference can be eliminated if the photometric titration is carried out in a phosphoric acid medium of 7·5*M* or above. The photometric method of titration is advantageous compared with the potentiometric one because chloride, nitrate, cerium(III) and manganese(II) ions do not interfere.

Procedure for iron(II) and vanadium(IV)

Use the same apparatus as before but pass carbon dioxide through the sample solution for 10 min *before* adding the phosphoric acid; this is done to remove oxygen dissolved in the sample solution. Titrate and plot the results as before. There is an initial increase in absorbance as a result of production of chromium(III) in the preferential oxidation of iron(II), followed by a decrease as the vanadium(IV) is oxidised: the absorbance finally becomes constant. The first point of intersection (Fig. 6) corresponds to the end-point for iron(II) and the second to that for vanadium(IV). Typical results are shown in Table IV and a titration curve in Fig. 6. The maximum relative error is 0·7% for both species.

Procedure for cerium(III)

Take 1–7 ml of cerium(III) solution (containing 15–100 mg of cerium) in the optical cell, add 30–33 ml of purified 90% syrupy phosphoric acid, and dilute to 40 ml with water. Stir with carbon dioxide as already described, and titrate with 0·1*N* potassium dichromate photometrically at 450 mμ (or with a blue filter). Measure the absorbance 1 min after each addition of titrant, and apply a correction for dilution. Some typical results are shown in Table V and a titration curve in Fig. 7. The maximum relative error is 0·6%. The absorbance of the chromium(III) and cerium(IV) increases slowly up to the end-point, and then there is a steep rise in absorbance, from the addition of excess of chromium(VI).

TABLE III.

Foreign ion	Amount added, *mg*	Vanadium(IV) found,* *mg*
Chloride (as KCl)	596	22·32
Chloride (as KCl)	1491	22·32
Chloride (as KCl)	2982	22·37
Nitrate (as NH_4NO_3)	800	22·32
Nitrate (as NH_4NO_3)	1600	22·37
Nitrate (as NH_4NO_3)	3200	22·37
Cerium(III)	70	22·27
Cerium(III)	140	22·21
Manganese(II)	37	22·27
Manganese(II)	74	22·21
Cobalt(II)	33	22·37
Cobalt(II)	66	22·42
Nickel(II)	38	22·32
Nickel(II)	76	22·32
Molybdenum(VI)	96	22·27
Uranium(VI)	116	22·27
Chromium(III)	20	22·21
Zinc(II)	65	22·21
Iron(III)	56	22·32

* Vanadium(IV) taken: 22·32 mg.

TABLE IV.—PHOTOMETRIC TITRATION OF A MIXTURE OF IRON(II) AND VANADIUM(IV) WITH POTASSIUM DICHROMATE IN A 3*M* PHOSPHORIC ACID MEDIUM

Iron(II), *mg*		Vanadium(IV), *mg*	
Taken	Found	Taken	Found
8·94	8·88	9·23	9·17
11·31	11·28	9·75	9·78
15·75	15·75	10·53	10·59
17·60	17·60	18·27	18·40
21·71	21·67	21·45	21·58
26·70	26·86	29·38	29·29

TABLE V.—PHOTOMETRIC TITRATION OF CERIUM(III) WITH POTASSIUM DICHROMATE IN A 10·5*M* PHOSPHORIC ACID MEDIUM

Cerium(III), *mg*	
Taken	Found
15·43	15·43
22·64	22·64
25·64	25·53
44·23	44·47
46·20	46·20
57·51	57·84
64·10	64·42
76·70	76·63
87·56	87·84
94·71	95·17

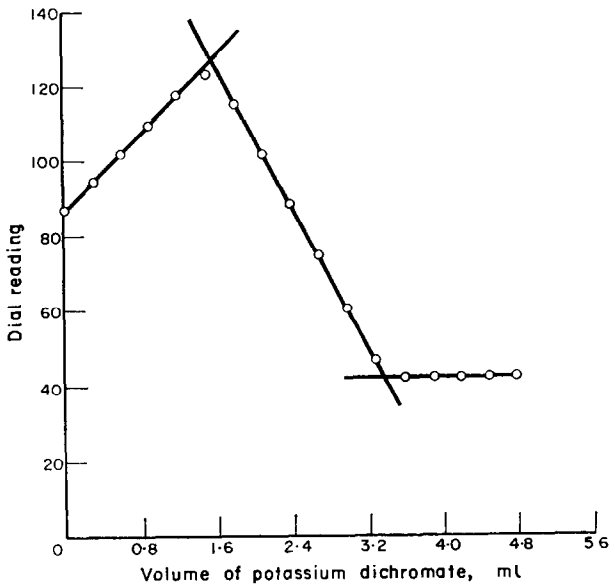

FIG. 6.—Photometric titration of a mixture of iron(II) (17·60 mg) and vanadium(IV) (18·27 mg) with 0·2*N* potassium dichromate in a 3*M* phosphoric acid medium.

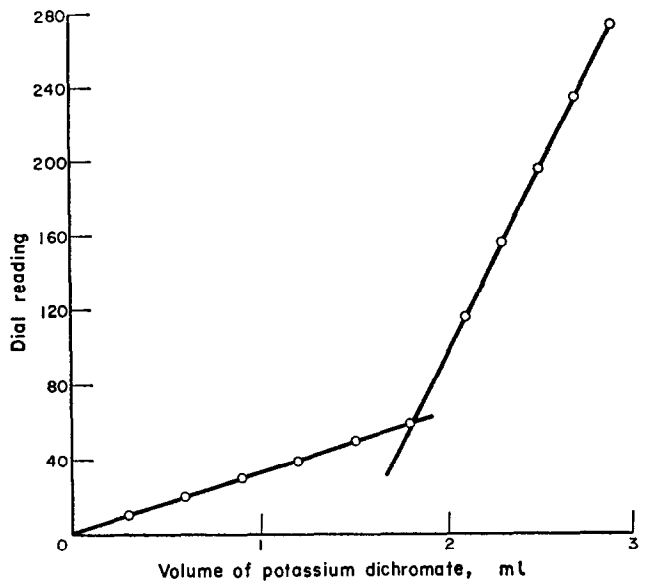

FIG. 7.—Photometric titration of cerium(III) (25·64 mg) with 0·1*N* potassium dichromate in a 10·5*M* phosphoric acid medium.

Interferences

Iron(II), vanadium(IV), manganese(II), arsenic(III), antimony(III), uranium(IV) and molybdenum(V) are also oxidised by potassium dichromate under the conditions proposed for the photometric titration of cerium(III). However, a separate equivalence point can be obtained from the titration curve when iron(II) is present with cerium(III) (see later). Fluoride, which forms a precipitate with cerium(III), also interferes. Chromium(III) interferes slightly if the titration is started immediately after adding phosphoric acid because any chromium(III) salt other than phosphate has some absorption in the region where chromium(VI) also absorbs; moreover this absorption of chromium(III) does not remain constant but changes with time because of increasing complexation with phosphoric acid. If the mixture of salts and phosphoric acid is kept for 2 hr equilibration of phosphoric acid with chromium(III) is almost complete and the titration with potassium dichromate can then be started without any interference from chromium(III). Although cobalt(II), nickel(II), molybdenum(VI), uranium(VI) and cerium(IV) have some absorption in the same region as chromium(VI), they do not interfere because this absorption remains constant throughout the experiment. Thallium(I) and large quantities of chloride do not interfere. The non-interference of chloride is an advantage of the photometric method over the potentiometric titration. Nitrate slowly oxidises cerium(III) in a strong phosphoric acid medium and interferes. Sulphuric acid does not interfere even up to a concentration of 1*N*. Iron(III), thallium(I), copper(II), zinc(II), tungsten(VI), thorium(IV), *etc.*, do not interfere (Table VI).

TABLE VI.

Foreign ion	Amount added, *mg*	Cerium(III) found,* *mg*
Chloride (as KCl)	745	42·03
Chloride (as KCl)	1490	42·03
Chloride (as KCl)	2980	44·13†
Cobalt(II)	64·45	41·47
Nickel(II)	65·73	41·47
Iron(III)	55·85	41·75
Chromium(III)	13·00	41·75
Molybdenum(VI)	95·95	41·61
Uranium(VI)	59·90	41·61
Cerium(VI)	140·0	42·03
Thallium(I)	51·10	41·61
Tungsten(VI)	86·80	41·75
Copper(II)	63·57	41·61
Thorium(IV)	116·0	41·47
Zinc(II)	65·38	41·61

* Cerium(III) taken: 41·75 mg.
† Interferes.

Procedure for iron(II) and cerium(III)

Perform the titration as described for cerium(III) alone. The iron(II) is preferentially oxidised, and the absorbance increases slowly, the absorbing species being the chromium(III) produced. When the iron has all been oxidised the absorbance increases slightly more rapidly [chromium(III) and cerium(IV)] until after the cerium end-point, when the excess of chromium(VI) absorbs strongly. Because of the low molar absorptivity of the chromium(III) and cerium(IV) the first end-point is difficult to interpret (Fig. 8), and errors made here affect both the iron and the cerium results, the errors being in opposite directions. Consequently the relative error (as is evident from the typical results in Table VII) is rather large, about 2%. A better accuracy can be attained by determining the total titre photometrically by the method described, and titrating the iron(II) separately with potassium dichromate in 0·5*M* sulphuric acid, using barium diphenylamine sulphonate as indicator. Under these conditions the cerium(III) is not titrated, and its titre is found by difference. Results obtained in this way are shown in Table VIII; the relative errors here are 0·4% for iron and 1·0% for cerium.

Analysis of cerium in a mineral

Digest about 10 g of sample (*e.g.*, monazite sand) in a porcelain evaporating dish with 25 ml of concentrated sulphuric acid on a sand-bath until most of the sulphuric acid is evaporated. Cool, leach the mass with 1*M* sulphuric acid, filter and dilute to 250 ml in a volumetric flask. Withdraw 8-ml portions and titrate them by the procedure described for cerium(III). The rare earths and thorium do not interfere. Typical results for a monazite sand from Travancore are shown in Table IX.

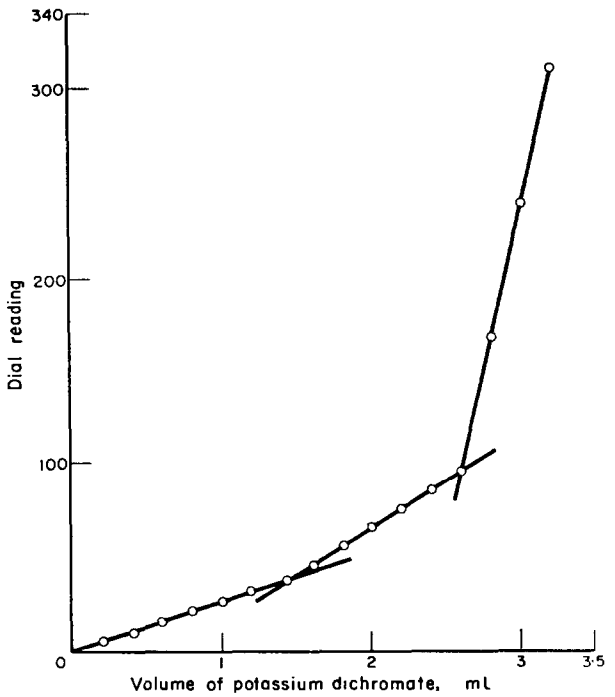

FIG. 8.—Photometric titration of a mixture of iron(II) (15·74 mg) and cerium(III) (33·29 mg) with 0·2*N* potassium dichromate in a 10·5*M* phosphoric acid medium.

TABLE VII.—PHOTOMETRIC TITRATION OF A MIXTURE OF IRON(II) AND CERIUM(III) WITH POTASSIUM DICHROMATE IN 10·5*M* PHOSPHORIC ACID

Iron(II), *mg*		Cerium(III), *mg*	
Taken	Found	Taken	Found
7·23	7·33	51·70	51·23
11·62	11·50	65·93	66·74
15·74	15·86	33·29	32·96
18·77	18·41	18·10	18·43
24·10	24·22	30·54	30·54
30·28	29·98	64·05	64·65

TABLE VIII.

Iron(II), *mg*		Cerium(III), *mg*	
Taken	Found	Taken	Found
7·23	7·26	51·70	51·30
11·62	11·61	65·93	65·55
15·74	15·75	33·23	33·34
18·77	18·70	18·10	18·28
24·10	24·10	30·54	30·26
30·28	30·28	64·05	64·15

The method now developed for the photometric titration of cerium(III) is more convenient than the method of Bricker and Loeffler.[8] These workers employed cobalt(III) sulphate for the photometric titration of cerium(III) in a 1*M* sulphuric acid medium using silver nitrate as catalyst, and measured the absorbance at 400 mμ [cerium(IV)] or at 610 mμ [cobalt(III)]. Cobalt(III) sulphate is difficult

TABLE IX.—ANALYSIS OF CERIUM IN MONAZITE SAND*

Cerium found, %	
New method	Method of Willard and Young[7]
24·15, 24·15, 24·30 Mean 24·20	24·09, 24·20, 24·16 Mean 24·15

* Iron(II) content is negligible.

to prepare and is unstable in aqueous solution at room temperature. Further, the dichromate method now proposed by us is subject to fewer interferences. Chromium(III), chloride, acetic acid and oxalic acid do not interfere in the dichromate method, whereas they interfere in the cobalt(III) method. The photometric titration of cerium(III) in a neutral pyrophosphate medium with potassium permanganate proposed by Marple, Przybylowicz and Hume[9] requires close control of pH (5·5–7·0). If the pH is high, basic salts may precipitate and if it is low the stoichiometry of the reaction is altered because of incomplete stabilisation of the reduced manganese in the tervalent state. Moreover, this method is subject to more interferences than the dichromate method proposed by us.

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Zusammenfassung—Vanadium(IV) kann mit Kaliumdichromat in Medien, die 3–12*M* Phosphorsäure enthalten, genau titriert werden: bei Gebrauch eines Rotfilters wird die Änderung der Absorption von Vanadium(IV) im Bereich von 660 nm verfolgt. Es ist bequemer, die Titration in 3 M Phosphorsäure auszuführen, da bei höherne Konzentrationen Chlorid, Nitrat, Cer(III) und Mangan(II) stören können. Photometrische Titration ist bequemer als potentiometrische, da erstere in 3*M* Phosphorsäure stattfinden kann, letztere dagegen nur in 12*M* Phosphorsäure möglich ist. Die gleichzeitige differenzphotometrische Titration von Eisen(II) und Vanadium(IV) ist auch möglich. Die Bedingungen für die photometrische Titration von Cer(III) und Cer(III) plus Eisen(II) wurden gefunden. Die Titration wird (bei 450 nm oder mit Blaufilter) in etwa 10,5*M* Phosphorsäure durchgeführt. Die Anwending der Vorschrift auf ein Cermineral wird erörtert.

Résumé—On peut doser avec précision le vanadium(IV) au moyen de bichromate de potassium dans des milieux contenant de l'acide phosphorique à la concentration 3–12*M*: on suit la variation d'absorption du vanadium(IV) dans la région 660 mμ en utilisant un filtre rouge. Il est plus convenable de mener le dosage en acide phosphorique 3*M* car, aux plus fortes concentrations, chlorure, nitrate, cérium(III) et manganèse(II) peuvent interférer. Le dosage photométrique convient mieux que le dosage potentiométrique car le premier peut être effectué en milieu acide phosphorique 3*M*, alors que le second n'est possible

qu'en acide phosphorique 12*M*. Le dosage photométrique différentiel simultané du fer(II) et du vanadium(IV) est également possible. On a trouvé des conditions de dosage photométrique du cérium(III) et de cérium(III) plus fer(II). Le dosage est mené (à 450 mμ ou avec un filtre bleu) en acide phosphorique environ 10,5*M*. On considère l'application de la méthode à un minéral du cérium.

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SEPARATION OF STRONTIUM FROM LARGE AMOUNTS OF CALCIUM, WITH APPLICATION TO RADIOSTRONTIUM ANALYSIS

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Summary—The elution first of calcium and then of strontium by complex formation with cyclohexanediaminetetra-acetic acid (CyDTA) after sorption on ion-exchange columns, is shown to require careful control of pH and the concentrations of CyDTA and NH_4^+. A procedure is described for volumetric analysis of calcium and strontium, and for use of this separation procedure before determination of ^{90}Sr in sea-water. Careful choice of reagents and materials is shown to be necessary for use of such a method in determination of trace amounts of radiostrontium.

THE chemical separation of strontium from sea-water is complicated by the high concentration of calcium, which has a close chemical similarity to strontium. Numerous precipitation, extraction or ion-exchange procedures have been described for the separation or determination of strontium in materials containing calcium.[1–18] Of these, most are not suitable for treatment of large volumes of sea-water; those which have been devised specifically for this purpose[1,12–14,16,17] are all time-consuming, of only moderate efficiency, and involve some steps which are potentially hazardous.

In searching for an improved method of collecting fallout ^{90}Sr from large volumes of sea-water, we have developed an ion-exchange procedure using the complexing agent cyclohexanediaminetetra-acetic (CyDTA) to separate calcium from strontium. The procedure is free from hazardous chemicals, and is much less laborious than others we have used.

Wade and Seim[4] have discussed the reaction between a metal ion and the complexing agent EDTA. They have indicated that the system $M^{2+} + H_2Y^{2-} = MY^{2-} + 2H^+$ is dependent on the hydrogen ion concentration. As the acidity of a solution is increased, the concentration of the metal-EDTA complex will decrease; the concentration of the complex at any pH depends on its stability constant. On this basis, procedures using cation-exchange resins have been proposed for separation of calcium from strontium, followed by strontium determination by instrumental or chemical means.[3–8,11] A resin will in general favour retention of ionic species of smallest ionic radius (for a mixture of hydrated ions with the same charge); strontium can be retained and calcium eluted if a proper choice of conditions and complexing agent is made (the calcium complex is considerably more stable than the strontium complex).

The logarithms of the stability constants of the calcium and strontium complexes with EDTA are 10·59 and 8·63, respectively.[19] Comparable values for the stability constants with CyDTA, quoting from unpublished data, are 12·3 and 10·0.[19] The ratios between the stability constants of calcium and strontium with EDTA or CyDTA

are approximately the same, but the higher absolute values with CyDTA indicate that these complexes will compete more successfully with the resin than do the EDTA complexes. In ion-exchange complexing-agent elutions, we have found very important the combined effect of pH, concentration of complexing agent and concentration of additional cations; these three variables interact to affect the separation of calcium from strontium.

The procedure described is being used both for separation of strontium from as much as 55 l. of sea-water, and for the separate determination of strontium and calcium in mixed carbonate precipitates. In the measurement of ^{90}Sr at the low concentrations typical of deep ocean water, careful choice of reagents and materials is essential to minimize blank corrections.

EXPERIMENTAL

Resin capacity

Reagents and equipment. Dowex 50-X12 (50–100 mesh) cation-exchange resin washed with six 50-ml portions of 6*M* hydrochloric acid, then with water followed by 10% ammonium chloride solution until the washings were neutral, finally with water until tests showed no chloride present. Calcium acetate solution, 10% w/w, adjusted to pH 4·7 with ammonia and acetic acid. Glass column: 1·2 × 20 cm fitted with a glass-wool plug and teflon stop-cock.

Procedure. The washed resin was filtered under suction and dried in an oven at 70° for 10 min. Then 3·6 g of the resin were slurried with water and transferred to the column. The calcium acetate solution was percolated through the column at a rate of 1 drop/2 sec. After breakthrough occurred, as indicated by testing the effluent with sodium carbonate, the column was washed with water and the calcium stripped from the column with 3*M* hydrochloric acid, precipitated as calcium carbonate, collected, and weighed to determine the resin capacity. This was 60 mg of calcium per g of dried resin.

Conditions for strontium elution

Reagents and equipment. Strontium chloride solution containing 11 mg of strontium per ml; ^{85}Sr tracer added to bring the specific activity of the solution to 500 cpm ^{85}Sr/mg Sr. CyDTA, 0.038*M*, prepared by dissolving 13.1 g of CyDTA in 300 ml of 1*M* ammonia and diluting to 1 l. Radiometer pH meter. Sodium iodide well-type scintillation counter. Ion-exchange columns prepared as already described.

Procedure

Elution of strontium at pH 6·7. Aliquots of the tagged strontium solution (5 ml) were sorbed on each of 4 columns. The CyDTA solution was adjusted to pH 6·7 with ammonia and acetic acid, and diluted and adjusted to give CyDTA concentrations of 0·028 and 0·018*M* with ammonium ion concentration 0·3*M*. Ammonium acetate, 0·3*M*, was adjusted to pH 6·7. Each of these solutions was used to elute strontium; 5-ml fractions of effluent, collected serially, were counted to obtain the elution curves shown in Fig. 1. The 0·028*M* CyDTA was the most efficient eluent.

Ammonium ion effect at pH 6·7 *and* 5·1. Solutions of 0·028*M* CyDTA were prepared, 1·1, 0·3 and 0·04*M* in ammonium ion at pH 6·7; 150 ml of each solution were passed through a column loaded with 5 ml of tagged strontium solution. The effluent was analysed for ^{85}Sr as before. The results are shown in Fig. 2. The experiment was repeated with solutions of 0·028*M* CyDTA, 0·2, 0·4, 0·8, 1·2, 1·6 and 2·0*M* in ammonium ion, and at pH 5·1. The results are shown in Fig. 3.

Effect of pH. The effect of varying the pH while keeping the CyDTA and ammonia concentrations constant at 0·028*M* and 0·3*M* respectively, is shown in Fig. 4.

From these results it is evident that at pH 6·7 the minimum ammonium ion concentration necessary for elution of strontium lies between 0·04 and 0·3*M*. At pH 5·1 the ammonium ion concentration must be below 0·4*M* to retain strontium on the column. With 0·028*M* CyDTA and 0·3*M* ammonium ion, complete retention of strontium on the column was observed at pH 5·0–5·5; partial elution occurred at pH 5·5–6·2, and at pH 6·2 strontium was completely eluted. Calcium was completely removed from the column by 0·028*M* CyDTA that was 0·3*M* in ammonium ion and at pH 5·1, and no detectable ^{85}Sr was present in the eluate.

Column loading characteristics

Some solutions containing 4·5, 8·5, 12·5 and 20·5 mg Sr/ml at pH 4·5 were passed at 7 ml/min through columns containing 3·6 g of resin, to find the concentration that gave maximum uptake. The best uptake occurred when the strontium concentration did not exceed 8·5 mg/ml.

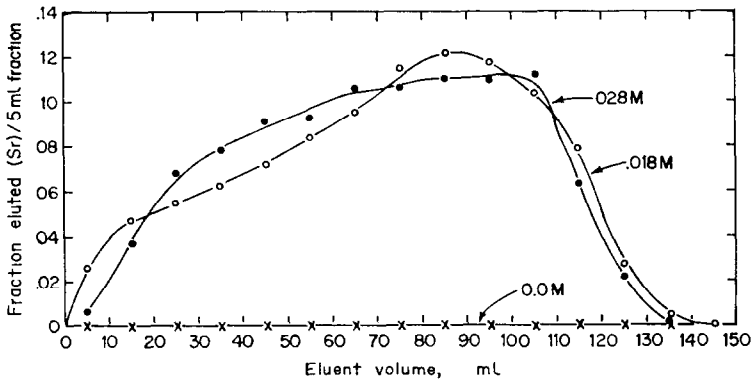

FIG. 1.—Strontium elution curves for 0·3*M* NH_4^+ at pH 6·7 and various CyDTA concentrations.

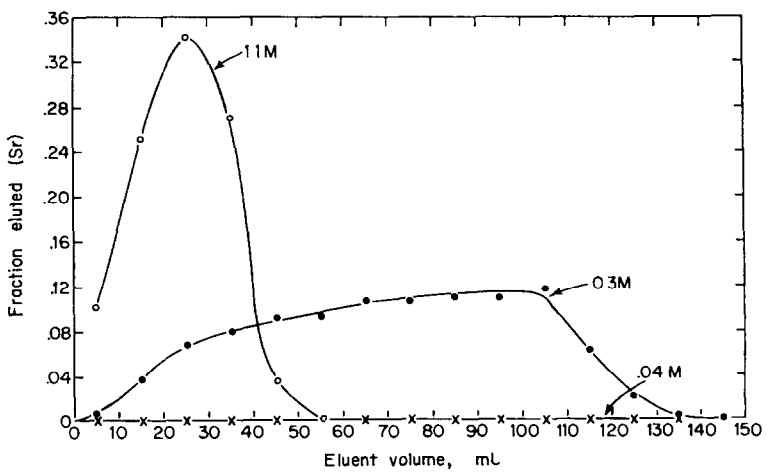

FIG. 2.—Strontium elution curves for 0·0286*M* CyDTA at pH 6·7 and various ammonium ion concentrations.

Sea-water samples

Separation of ^{90}Sr *from 500 ml of sea-water.* Fill a 1·2 × 55 cm glass column to a height of 31 cm with pretreated Dowex 50 resin (7·5 g of dry resin). Convert the resin to the ammonium ion form with 1*M* ammonium chloride and rinse it with water. With constant stirring acidify the sea-water sample to pH 1·0 with hydrochloric acid and add 100 mg of carrier strontium, and other desired carriers. Stir for several hr to ensure radiochemical equilibration. Adjust the sea-water to pH 7 with ammonia solution. Precipitate strontium, calcium, magnesium, barium and other interfering cations by adding sodium carbonate. Separate the strontium and much of the calcium by procedures described elsewhere.[1] Precipitate the mixed strontium-calcium carbonates; dry, weigh and dissolve them in a minimum amount of hydrochloric acid. Dilute the solution to give a concentration equivalent to 14 mg of the mixed carbonates per ml, and buffer to pH 4·7 with ammonia and acetic acid, maintaining the ammonium ion concentration in the final solution at 0·4*M*. Pass this solution through the column at 1 drop/2 sec; wash the column with 100 ml of water, and then at the same flow-rate elute calcium with a solution of 0·03*M* CyDTA and 0·4*M* ammonium ion buffered to pH 5·1. Test the effluent periodically with a saturated solution of oxalic acid. When no further precipitation is observed, stop the elution. Elute strontium with 0·03*M* CyDTA and 0·4*M* ammonium ion buffered to pH 6·7. Follow the course of elution by adding oxalate to each 10-ml portion, discontinuing

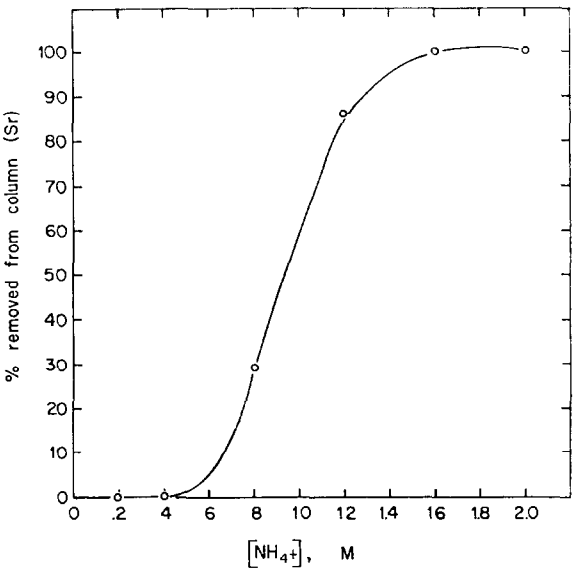

FIG. 3.—Elution of 55·8 mg of strontium with 150 ml of 0·028*M* CyDTA at pH 5·1 and various ammonium ion concentrations.

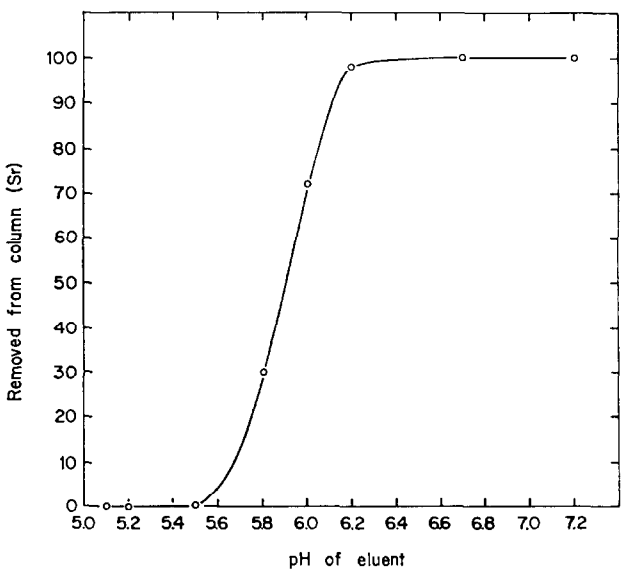

FIG. 4.—Effect of pH of eluent on elution of 55·8 mg of strontium with 150 ml of 0·028*M* CyDTA and 0·3*M* NH_4^+.

elution when no further precipitation is evident. Convert all the strontium oxalate into the carbonate and weigh it to determine recovery.

Separation of ^{90}Sr from 55 l. of sea-water. Prepare a 7 × 39 cm column with 1 lb of pretreated Dowex 50-X12 (50–100 mesh). Follow the procedure for ^{90}Sr in sea-water, described by Sugihara *et al.*[1] through the precipitation of mixed carbonates in the presence of EDTA. Weigh this precipitate, dissolve it in the minimum of hydrochloric acid needed and dilute with distilled water to a concentration of 14 mg of the mixed carbonates per ml; adjust the pH to 4·7 with ammonia and acetic acid, maintaining the ammonium ion concentration at 0·4*M* in the final solution. In routine operation, this results in volumes of about 2 l. Pass the solution through the resin column at 3 ml/min, rinse the column (500 ml of water) and strip calcium with the eluent described above (at 3 ml/min), checking the effluent periodically with oxalate (typically, 4–6 l. of effluent are needed for complete calcium elution). Next strip the strontium with the eluent described for 500-ml sea-water samples but at a flow-rate of 3 ml/min. If the stripping is not to be monitored or allowed to proceed overnight, 3*M* hydrochloric acid should be used as the stripping solution. If CyDTA is allowed to elute strontium unchecked, a large excess of it will be present in the effluent. The precipitation of strontium from this solution will be difficult and a loss in recovery evident. Precipitate strontium oxalate to determine recovery.

Separation and determination of strontium and calcium from their mixed carbonates. Dissolve the mixed carbonates in the minimum of hydrochloric acid needed, heat to expel carbon dioxide, and dilute to a known weight or volume. Remove an aliquot, adjust it to pH 9 with ammonia and titrate with standardized CyDTA (using Phthalein Purple indicator) to determine the total concentration of bivalent cations present. Load another aliquot onto a precleaned Dowex 50-X12 (50–100 mesh) column. The capacity of the column should exceed the sum of the calcium and strontium in the aliquot taken. Measure a volume of standardized CyDTA solution (pH 5·1, 0·4*M* in ammonium ion), corresponding to more than the total metal ion concentration on the column; pass it through the column at 3 ml/min, and follow it with two washes of water, each of about 1 column-volume. Determine calcium by titrating the excess of CyDTA in the combined eluent and washings with a standard calcium solution, using Phthalein Purple indicator. Then elute strontium as described above, again using a measured volume of CyDTA in excess of the strontium present, followed by two 1-column-volume water washes. Determine strontium by back-titration of the excess of CyDTA, as for calcium. A check is available in that the sum of the calcium and strontium found should equal the sum of calcium and strontium titrated in the first aliquot taken.

Determination of ^{90}Sr radiochemical blanks. Since this procedure was to be used for the determination of very low concentrations of ^{90}Sr in sea-water, reagent blanks were run to assess their radioactive contamination. Commercial cation-exchange resins have been shown[20] to contain small amounts of ^{90}Sr within the resin lattice, and these traces are not entirely removable by any continuous elution process. Slow release of strongly bound impurities during the interval between resin purification and use has also been noted.[21]

By the procedure outlined above for separation from 55 l. of sea-water, samples of commercial calcium and strontium salts were loaded on to columns and separated as shown in Table I. The eluted strontium in each case was weighed as carbonate to determine recovery, and then dissolved in 1*M* hydrochloric acid. After 15 days, iron(III) hydroxide was precipitated from this solution, dried, mounted and its beta-activity determined with a low-background detector. The net activity (Fig. 5) decreased with a 64·5 hr half-life, typical of the ^{90}Sr daughter, ^{90}Y.

The counting results (Table I) show that both calcium and strontium carbonates contain varying amounts of ^{90}Sr, whereas strontium chloride (at least the lot tested) is free of this isotope. Sample CB5 shows that some ^{90}Sr can be eluted from a large capacity Dowex 50-X12 column, even after precleaning as outlined above.

DISCUSSION

It appears that by careful choice of resins, carriers and other reagents, essentially no ^{90}Sr blank should be obtained with procedures proposed. Resin preparation and cleaning probably should be done with both hydrochloric and nitric acids; the fact that the distribution coefficient of barium is substantially lower in the nitric acid/cation-exchanger system than in the corresponding hydrochloric acid system,[22] suggests that the retention of ^{90}Sr on the resin may be reduced by nitric acid washing.

For routine analysis of ^{90}Sr in large numbers of samples containing large amounts of calcium, this separation method is an improvement in terms of speed, convenience and amount of sample manipulation, over the more conventional strontium–calcium separations by use of large quantities of fuming nitric acid.

TABLE I.—^{90}Sr RADIOCHEMICAL BLANKS

No.	Cation-exchange resin*	Sample composition	^{90}Sr *dis/min*
CB-1	A	$CaCO_3$, lot 1,† 50 g $SrCO_3$, lot 10, 5·0 g	7·4 ± 0.4
CB-3	A	$CaCO_3$, lot 2,† 50 g $SrCO_3$, lot 11, 5·0 g	4·6 ± 0·3
CB-2	B	$CaCO_3$, lot 1, 50 g $SrCO_3$, lot 10, 5·0 g	2·7 ± 0·2
CB-4	B	$CaCO_3$, lot 2, 50 g $SrCO_3$, lot 11, 5·0 g	3·3 ± 0·2
CB-5	B	$SrCl_2$, lot 12, 5·4 g	0·24 ± 0·12‡
CB-6	B	$CaCO_3$, lot 2, 50 g $SrCl_2$, lot 12,† 5·4 g	4·3 ± 0·3
Reagents		$SrCl_2$, lot 12,† 5·4 g $SrCO_3$, lot 10,† 5·0 g $SrCO_3$, lot 11,† 5·0 g $SrCO_3$, lot 13,† 5·0 g	not detectable 0·26 ± 0·07 0·19 ± 0·06 0·92 ± 0·30

* Dowex 50-X12 (50–100 mesh); A, lot unknown; B, lot 03093-WI-B12.
† Mallinckrodt Chemical Works.
‡ Chemical yield for this run was low because of accidental loss of sample. The *dpm* figure was calculated from a nett count-rate of 0·030 ± 0·015 cpm.

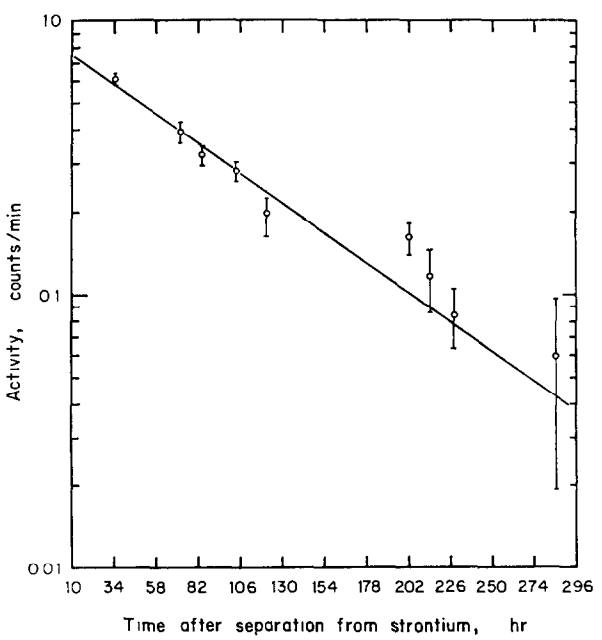

FIG. 5.—Decay curve of iron(III) hydroxide precipitate from a blank strontium solution (CB-2, Table I). Uncertainties indicated are $\pm\sigma$, from counting statistics only.

The average recovery of strontium from 500 ml of sea-water by CyDTA elution was found to be 75% for 50 samples; the 25% loss appeared to occur, indiscriminately, either before or after the elution chemistry.

More than 50 samples of mixed strontium and calcium carbonates (Sr:Ca ratio ranging from 0·1 to 0·8) have been analysed for strontium as described. The error associated directly and indirectly with the strontium determination in each sample averaged ±0·65% over the 50 samples.

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Zusammenfassung—Es wird gezeigt, daß die aufeinanderfolgende Elution von Calcium und Strontium durch Komplexbildung mit Cyclohexandiamintetraessigsäure (CyDTA) nach Sorption an Ionenaustauschersäulen genaue Kontrolle des pH und der Konzentrationen von CyDTA und NH_4^+ erfordert. Es wird ein Verfahren zur volumetrischen Bestimmung von Calcium und Strontium beschrieben mit Anwendung dieser Trennmethode vor der Bestimmung von ^{90}Sr in Meerwasser. Es wird gezeigt, daß sorgfältige Auswahl der Reagentien notwendig ist, um mit einer derartigen Methode Spuren von Radiostrontium zu bestimmen.

Résumé—On montre que l'élution du calcium puis du strontium par formation de complexe avec l'acide cyclohexanediaminotétracétique (CyDTA) après sorption sur colonnes échangeuses d'ions nécessite un contrôle minutieux du pH et des concentrations de CyDTA et NH_4^+. On décrit une technique pour l'analyse volumétrique du calcium et du strontium et pour l'emploi de cette méthode de séparation avant dosage de ^{90}Sr dans l'eau de mer. On montre qu'un choix minutieux des réactifs et des produits est nécessaire pour l'emploi d'une telle méthode dans le dosage du radiostrontium à l'état de traces.

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DETERMINATION OF RHENIUM IN MOLYBDENITE BY NEUTRON-ACTIVATION ANALYSIS*

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Summary—A neutron-activation method is described for the determination of rhenium in molybdenite. Radiochemical separation by a carrier technique was carried out very rapidly by means of successive liquid–liquid extraction processes. The recovery of rhenium, which was determined by a spectrophotometric method, was about 93%. About 10 samples could be analysed within 6 hr in parallel runs.

RHENIUM is an element of very low cosmic and terrestrial abundance. The distribution of the element in natural sources can be studied only by a very sensitive analytical method; of the techniques readily available neutron-activation analysis seems to be the most adequate. Neutron-activation analysis has been applied to the determination of rhenium in meteorites,[1,2] igneous rocks,[3] and minerals.[4,5] Various methods of radiochemical separation have been used in the procedures for rhenium, *viz.*, distillation,[6,7] precipitation,[8–12] ion-exchange chromatography[13–16] and liquid–liquid extraction.[17–21] Liquid–liquid extraction seems to be the most useful method because of its simplicity and rapidity. In some minerals such as molybdenite, rhenium occurs in association with a large amount of molybdenum. Therefore, in the activation-analysis of such molybdenum-rich minerals, ^{99}Mo is formed in an excessive amount after irradiation of ^{98}Mo (which occurs to the extent of 23·75% in nature) with a thermal neutron flux, and it must be completely removed from rhenium. Moreover, ^{99m}Tc and ^{99}Tc may be produced by β-decay of the ^{99}Mo with its half-life of 66·0 hr, so these should also be excluded. A number of studies have been made on the separation of rhenium from molybdenum and technetium, but it is still difficult to separate the former by liquid–liquid extraction.

Nuclear data

Nuclear data for the thermal neutron activation of rhenium have been summarized by Morris and Fifield.[3]

Rhenium analysis in the present work was based on the nuclides ^{186}Re and ^{188}Re which have half-lives, sufficiently long to survive both the transit time from the reactor site and the time required for chemical processing. It is assumed that their isotopic abundance is the same in all rhenium samples used. Although analyses based on ^{188}Re may suffer some interference[3] from a second order reaction of ^{186}W, 100 ppm of ^{186}W (abundance 28·4%) will produce an activity equivalent to less than 4×10^{-7} ppm of rhenium in an hour. Therefore, this interference may be ignored in the present work.

* Part of the work was performed at the Research Reactor Institute, Kyoto University, and the paper was read at the 9th Symposium in Radiochemistry, Chemical Society of Japan, at Hiroshima, 12 October 1965.

EXPERIMENTAL

Reagents

Standard rhenium solution: 0·1 g of 99·94% pure rhenium was dissolved in 1 ml of conc. nitric acid by heating on a water-bath, and the solution was neutralized with sodium hydroxide solution and diluted to 100 ml with distilled water. This stock solution was standardized gravimetrically via tetraphenylarsonium perrhenate and diluted to a suitable concentration for the standard sample and the carrier solution.

Radioactive rhenium solution: Rhenium-186 was prepared by neutron irradiation of rhenium metal and dissolved in the same way as the non-radioactive rhenium.

Molybdenum solution: Molybdenum trioxide was crystallized from ammonium molybdate solution treated with conc. hydrochloric acid, and was filtered off, washed, and heated at 600° for 5 hr in an electric furnace. Its purity was found to be 99·96% by reductimetric analysis. Forty g of it were dissolved in a small volume of 1N sodium hydroxide solution, and diluted to 500 ml with distilled water. This solution contained 54 mg of molybdenum/ml.

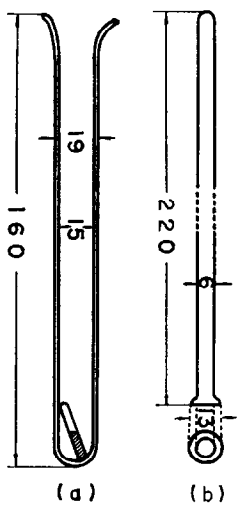

FIG. 1.—(a) Test-tube thickened at bottom; (b) Glass rod with flattened end.

Radioactive molybdenum solution: Molybdenum-99 was prepared by neutron irradiation of the molybdenum trioxide, and a solution of the product was made in the same way as the non-radioactive solution.

Apparatus

A Hitachi EPU-2A type spectrophotometer with 10-mm glass cells, a Horiba Model M-3 glass electrode pH meter, and a γ-ray scintillation counter (Kobe Kogyo Co.) consisting of a PS-400 scintillation probe (SG-78W, 1¾ in. dia. × 2 in. NaI(Tl) crystal) and an SA-230 "1000" scaler, were used. A 50-ml, spindle-shaped separating funnel and an Iwaki shaking-machine, type KM, were used.

Irradiation

A sample of about 0·1 g of the finely-ground molybdenite (about 100-mesh) was accurately weighed and sealed in a clean silica tube (4-mm bore). In a similar tube a standard was prepared by weighing about 0·01 ml of 100 ppm standard rhenium solution on to about 0·1 g of finely powdered quartz in the tube, drying, and sealing. Samples and standards were wrapped in aluminium foil, packed with cotton in a polyethylene capsule, and irradiated with a thermal neutron flux of 4×10^{12} n.cm^{-2}.sec^{-1} for periods of 1 hr in the nuclear reactor KUR, Research Reactor Institute, Kyoto University.

Radiochemical separation

After irradiation, the samples and standards were left to "cool" for 30 min and then assayed radiochemically for ^{186}Re and ^{188}Re. The silica tubes were removed from the capsule and foil, and transferred to a test-tube with a thickened bottom. The silica tubes were broken with a glass rod as shown in Fig. 1. Then 1 ml of conc. nitric acid was added in the glass tube and the solution was

heated in a boiling water-bath for 1 hr. The tubes were removed and 2 ml of Re carrier (250 ppm) and 3 ml of 10*N* sodium hydroxide were added. Any precipitate was removed by centrifugation.

The supernatant liquid was transferred to a 50-ml separating funnel; the residue was washed with 4 ml of distilled water, and the washings transferred to the separating funnel after centrifugation. Then 2 ml of 1% aqueous tetrabutylammonium hydroxide solution were added. The rhenium was extracted as perrhenate by shaking with 10 ml of methyl isobutyl ketone (MIBK) for 10 min; the lower layer was rejected and the organic extract was washed twice with 10-ml portions of 2*N* sodium hydroxide which contained 1 ml of 1% tetrabutylammonium hydroxide solution and 10% of sodium chloride.

The organic phase was then shaken for 10 min with two 10-ml portions of 0·25*M* sodium perchlorate which contained about 5% of sodium chloride. The aqueous extracts were combined in a brown-glass separating funnel and the organic (upper) layer was discarded.

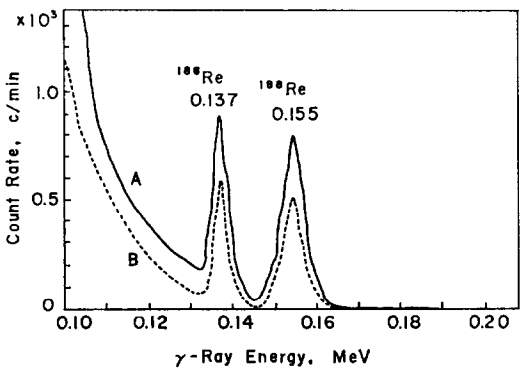

FIG. 2.—Gamma ray spectra of final solution:
A-standard; B-molybdenite sample.

Then 1 ml of conc. hydrochloric acid was added to make the final acid concentration about 0·5–0·6*N*, about 100 mg of potassium xanthate were added to the aqueous phase, and the technetium species was extracted by shaking with 10 ml of carbon tetrachloride for 30 min. The process was repeated and the organic phase discarded. Finally, the aqueous phase was washed with 5 ml of carbon tetrachloride and the organic washings were discarded.

The residual aqueous phase was transferred to a 25-ml standard flask and diluted to 25 ml with distilled water. Then 10 ml of this solution were transferred by pipette into another 25-ml standard flask, and 6 ml of conc. hydrochloric acid, 4 ml of 10% sodium thiocyanate solution and 3 ml of 20% tin(II) chloride solution were added, and the solution was diluted to 25 ml with water. After 30 min the absorbance of the coloured solution was measured at 378 mμ and the amount of rhenium calculated from a calibration curve. The standard and blank samples were treated in the same way.

Counting of the ^{186}Re *and* ^{188}Re

The final solutions were all counted with a well-type γ-ray scintillation counter. Five ml of the 25 ml of final sample solution were transferred to a polyethylene test-tube (12 mm i.d.) and counted. All activities were corrected for paralysis, background, and chemical yield, and decay measurements were made. After about 6 days the ^{188}Re activity had disappeared and subsequent decay was that theoretically expected for ^{186}Re. From the activity of samples and standards at any arbitrarily chosen time, the rhenium content of the original material could be found from the relationship:

$$\text{Weight of Re in sample} = \text{Weight of Re in standard} \times \frac{\text{Corrected counting rate of sample}}{\text{Corrected counting rate of standard}}.$$

The blank test for the powdered quartz used to make the standard gave a negligible counting rate.

Additional confirmation that ^{186}Re and ^{188}Re were the only radionuclides assayed was obtained by γ-ray spectrometry. Typical spectra are shown in Fig. 2.

RESULTS

In Table I are shown the results of the neutron-activation analysis of rhenium in two molybdenite samples from different sources in Japan. The paired values were obtained by irradiation at same time. The loss of rhenium in the dissolution and centrifugation processes was estimated to be below 0·5%.

TABLE I.—RHENIUM CONTENTS OF SOME MOLYBDENITES, DETERMINED BY NEUTRON-ACTIVATION ANALYSIS

	Hirase, Gifu, Japan	Seikyu, Shimane, Japan
Molybdenite Re, ppm	11·2 *	82·8 †
	11·4 *	81·4 †
	11·2 †	85·2 ‡
	11·3 †	86·2 ‡

* Irradiated on 23 June 1965.
† Irradiated on 20 July 1965.
‡ Irradiated on 21 October 1965.

DISCUSSION

Separation of rhenium from molybdenum by solvent extraction

Rhenium was completely separated from about 60 mg of molybdenum by solvent extraction. Maeck *et al.*[23] reported that rhenium(VII) was extracted into methyl isobutyl ketone from both acidic and alkaline solutions in the presence of tetrabutylammonium salts. According to their results, it seemed possible to separate rhenium from most other metals, including molybdenum. In the present study the alkaline MIBK system was chosen because several metal ions in the samples could be removed as their hydroxide precipitates before the extraction. Experiments were done to find the optimum conditions for extraction of rhenium, using ^{186}Re as a tracer.

Effect of the concentration of alkali on the extraction. Variation of the sodium hydroxide concentration from 0·5 to 5*M* was without effect, >99% of the rhenium (in amounts of 30–300 μg) being extracted; 2·0*M* alkali was therefore preferred. No change of the basicity of the aqueous phase occurred before or after the extraction.

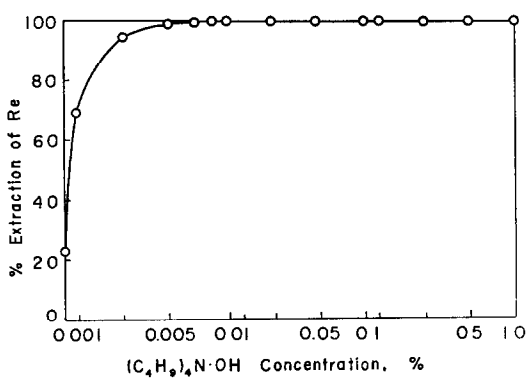

FIG. 3.—Effect of concentration of tetrabutylammonium hydroxide on the extraction of rhenium. Concentration of rhenium 50 ppm.

Effect of the tetrabutylammonium salt concentration. As shown in Fig. 3, >99% of the rhenium was extracted when the aqueous phase contained more than 0·01% of tetrabutylammonium hydroxide in 2·0*M* alkali. Rhenium was completely separated from 60 mg of molybdenum if the concentration of the reagent was in the range 0·025–1·0%.

The effect of other ions on the extraction. From the results of Maeck *et al.*, it seemed that relatively large amounts of pertechnetate, permanganate, osmium(IV), platinum(IV), gold(III) and mercury(II) ions might have some effect on the extraction of perrhenate, but, as shown in Table II, 10 mg of any of these ions was without effect.

TABLE II.—EFFECT OF OTHER IONS ON EXTRACTION OF RHENIUM WITH TETRABUTYLAMMONIUM SALTS

Ions	Added (*mg*/10 *ml*)	Recovery of Re in organic phase* (%)
Mo(VI)	60	99·9
Mn(II)	10	99·9
Mn(VI)	10	99·7
Fe(III)	10	99·8
Al(III)	10	99·9
Cr(III)	10	99·9
Cr(VI)	10	99·8
Co(II)	10	99·8
Cu(II)	10	99·9
Ni(II)	10	99·9
Zn(II)	10	99·8
Cd(II)	10	99·9
Zr(IV)	10	99·8
V(V)	10	99·9
W(VI)	10	99·9
Ag(I)	10	99·9
Pt(IV)	10	99·9
Au(III)	10	99·9
Hg(II)	10	99·8
Ru(VI)	10	99·9
Os(III)	10	99·8
U(VI)	10	99·8
Th(IV)	10	99·8
Se(IV)	10	99·9

* 50 ppm of Re were present in each run.

The amounts of these elements in ordinary rocks or minerals would not affect the extraction of rhenium.

In Table III, the effect of several anions is shown. Perchlorate and thiocyanate interfere seriously, iodide and chlorate interfere to a lesser extent. Perchlorate and thiocyanate presumably interfere by competing with perrhenate in ion-pair formation with the quaternary ammonium ions; this property can be used to good effect in the back-extraction process.

Back-extraction of rhenium into the aqueous phase. The rhenium in MIBK must be back-extracted to separate it from technetium. The results obtained with sodium

perchlorate and perchloric acid solutions of varying concentration are shown in Fig. 4. According to Gerlit,[21] perrhenate can be extracted fairly well into MIBK from acidic solution ($K_d = 3{\cdot}8$ from $2N$ sulphuric acid). The decrease in the amount of rhenium back-extracted as the concentration of perchloric acid increased, may be attributed to this behaviour.

Addition of sodium chloride was found to improve the separation of the phases. A composite reagent containing $0{\cdot}5M$ perchlorate was found satisfactory and to give >99% recovery of rhenium in two extractions.

A small amount of MIBK was often transferred with the aqueous phase and interfered in the spectrophotometric determination, but could be readily removed by back-washing the aqueous phase with carbon tetrachloride.

TABLE III.—EFFECT OF ANIONS ON EXTRACTION OF RHENIUM WITH TETRABUTYLAMMONIUM SALTS

Anions	Concentration, M	Recovery of Re in organic phase* (%)
Cl^-	0·50	99·9
	1·00	99·9
Br^-	0·125	99·7
	0·25	99·8
I^-	0·025	98·9
	0·06	95·2
	0·125	90·5
	0·25	83·7
SCN^-	0·006	99·2
	0·012	96·5
	0·025	90·5
	0·06	76·3
	0·125	61·3
	0·25	42·7
	0·50	17·5
ClO_3^-	0·125	98·8
	0·25	97·6
BrO_3^-	0·125	99·8
	0·25	99·8
IO_3^-	0·125	99·9
	0·25	99·8
NO_3^-	0·25	99·7
	0·50	96·7
ClO_4^-	0·125	9·9
	0·25	5·6
	0·50	2·3
SO_4^{2-}	0·50	99·9
	1·00	99·8
PO_4^{3-}	0·25	99·9
	0·50	99·9
CH_3COO^-	0·25	99·9
	0·50	99·9

* 50 ppm of rhenium were present in each run.

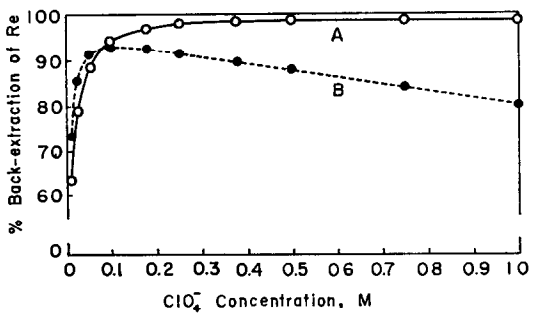

FIG. 4.—Effect of concentration of perchlorate and perchloric acid on back-extraction of rhenium.
A—Sodium perchlorate; B—Perchloric acid. Concentration of rhenium 50 ppm.

Separation of rhenium and technetium nuclides. The radionuclide 6 hr ^{99m}Tc (γ, 0·1403 MeV) may be produced during or after the neutron-irradiation of molybdenite by the following processes:

$$^{98}\text{Mo}(n, \gamma)^{99}\text{Mo} \xrightarrow[t_{\frac{1}{2}}=66\text{ hr}]{\beta^-} {}^{99m}\text{Tc}$$
$$^{98}\text{Tc}(n, \gamma)^{99m}\text{Tc}$$
$$^{99}\text{Tc}(n, n)^{99m}\text{Tc}$$
$$^{99}\text{Ru}(n, p)^{99m}\text{Tc}$$

The first process may predominate in this case, and this nuclide will certainly interfere considerably in the γ-counting of the rhenium activity.

It was observed that a considerable activity of ^{99m}Tc had been produced as expected, and remained after the molybdenum had been removed by the first extraction. Rhenium had been separated from technetium by solvent extraction[24] with xanthate into carbon tetrachloride; double extraction with rather larger amounts of xanthate (100 mg in each extraction) proved satisfactory.

Spectrophotometric determination of rhenium. This was used to determine the chemical yield of rhenium instead of the usual gravimetric method. The rhenium-tin(II)-thiocyanate complex gave absorption peaks at 378 and 420 mμ. The second peak has been used for the colorimetric determination of rhenium, but the absorbance at that wavelength varies considerably with time. The first peak was found to be useful since its absorbance obeyed Beer's law in the range of 0·0–12 ppm of rhenium. The colour of the solution was stable for at least 2 hr under the conditions recommended.[25] The error was found to be 1% over the range 1–12 ppm and 2% for about 0·5 ppm of rhenium.

Possible interferences. Morris and Fifield[3] and Morgan[5] reported possible interferences in the neutron-activation analysis of rhenium in various minerals and rocks. Most metal ions encountered in geological materials, *e.g.*, iron, manganese and chromium, could be removed by the procedure described above and the effect of these ions may be disregarded. The neutron self-shielding in the sample is insignificant because of the small size of sample used.

The mean chemical recovery of the added carrier was about 93%, and the time required for a complete radiochemical analysis of 10 samples was about 6 hr.

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Zusammenfassung—Ein Neutronenaktivierungsverfahren zur Bestimmung von Rhenium in Molybdänit wird beschrieben. Die radiochemische Abtrennung mittels Träger wurde mit Hilfe aufeinanderfolgender flüssig-flüssig-Extraktionsprozesse sehr schnell ausgeführt. Die Ausbeute an Rhenium, das spektrophotometrisch bestimmt wurde, betrug etwa 93%. Zehn Proben konnten in sechs Stunden in nebeneinanderlaufenden Arbeitsgängen bestimmt werden.

Résumé—On décrit une méthode par activation de neutrons pour le dosage du rhénium dans la molybdénite. La séparation radiochemique par une technique par entraînement a été menée très rapidement au moyen de méthodes d'extractions successives en phase liquide. La récupération du rhénium, déterminée par une méthode spectrophotométrique, est d'environ 93%. En menant les opérations en paralléle, on peut analyser environ 10 échantillons en 6 h.

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ELEKTRONISCHES RECHNEN IN DER ANALYTISCHEN CHEMIE—I

ALGOL-PROGRAMM FÜR DIE AUSWERTUNG VON MODELLANALYSEN

G. GOTTSCHALK
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Zusammenfassung—Ein üblicher Weg zur Ermittlung von Kenngrößen analytischer Verfahren ist die Durchführung einer Reihe von Modellanalysen. Über den Vergleich von bekannten vorgegebenen Mengen mit wiedergefundenen Mengen liefert eine geeignete Auswertung objektive ziffernmäßige Informationen über die zufälligen und systematischen Fehler in einem festgelegten Arbeitsbereich. Zeitbedarf und Schwierigkeitsgrad einer solchen Auswertung sind bei Verwendung konventioneller Rechentechniken relativ groß. So werden für eine Testreihe von 24 Modellanalysen ohne Berücksichtigung menschlich bedingter Rechenfehler mindestens 8 Std benötigt. Erfahrungsgemäß sind bei rechnerisch weniger geübten Personen oft sogar mehrere Tage erforderlich. Praktisch rechenfehlerfreie Resultate können dagegen bei elektronischer Datenverarbeitung in weniger als 5 min erhalten werden. Hierzu wird im folgenden ein Rechenprogramm in der problemorientierten Universalsprache ALGOL formuliert. Die verbleibenden vorbereitenden Arbeitsgänge sind bei dieser Form der Auswertung so einfach, daß sie von jeder Hilfskraft einwandfrei durchgeführt werden können.

VERWENDETE BEGRIFFE UND SYMBOLE (ALGOL-SYMBOLE IN KLAMMERN)

Gesamtanzahl der Testanalysen	n	(N)
Gruppenumfang	l	(—)
Laufzahlen, Einzelgrößen	i	(I)
Gruppengrößen	J	(—)
Umrechnungsfaktoren, für Einwaagen	λ_1	(L1)
für Meßwerte	λ_2	(L2)
Integralgrenzen t der t-Verteilung	t	(T)
Einwaagen an Standardsubstanz	G_1	(G[I])
Meßwerte (Auswaagen oder Volumina)	W_1	(W[I])
Vorgegebene Mengen	$[a_1]$	(VA)
Wiedergefundene Mengen	a_1	(WA)
Korrigierte wiedergefundene Mengen	$a_{\mathrm{K}i}$	(—)
Unkorrigierte Abweichungen	B_1	(—)
Zufällige Abweichungen	v_1	(ABW)
Variationskoeffizient	VK	(—)
Standardabweichung	$[s_{\mathrm{K}}]$	(SK)
Absolutkorrektur, Wert	$[U]$	(U)
Absolutkorrektur, mittlerer Fehler	$[s_{\mathrm{U}}]$	(SU)
Relativkorrektur, Wert	$[R]$	(R)
Relativkorrektur, mittlerer Fehler	$[s_{\mathrm{R}}]$	(SR)
Prüfgrößen	τ	(TAU)

EINFÜHRUNG

ALS Modellanalysen sollen im folgenden quantitative analytische Bestimmungen aus dem Bereich der Gravimetrie und Titrimetrie bezeichnet werden, bei denen der Umrechnungsfaktor λ von der Meßgröße W_1 auf die Mengengröße a_1 von vornherein bekannt ist. Neben diesen auch „chemische Analysenverfahren" genannten Methoden gibt es eine Vielzahl „physikalischer Analysenverfahren", bei denen die zunächst unbekannten Umrechnungsgrößen durch Eichmessungen erst ermittelt werden müssen.

Die Auswertung von Modellanalysen beginnt mit Berechnungen vorgegebener Mengen $[a_1]$ aus Einwaagen G_1 einer Standardsubstanz sowie wiedergefundener Mengen a_1 aus Meßgrößen W_1 (Auswaagen, Volumina) mit Hilfe bekannter Umrechnungsfaktoren λ. Danach werden im allgemeinen absolute und relative Abweichungen ermittelt. Formelmäßig ergibt sich bei n Testanalysen der n-malige Handlungsvorgang:

Vorgegebene Menge	$[a_1] = \lambda_1 \cdot G_1$	mg	
Gefundene Menge	$a_1 = \lambda_2 \cdot W_1$	mg	
Abweichung, absolut	$B_1 = a_1 - [a_1]$	mg	(1)
Abweichung, relativ	$100 \dfrac{B_1}{[a_1]}$	Rel%	

wobei Laufzahl $i = 1, 2, \ldots, n$.

Anstatt der Mengeneinheit mg können auch andere Einheiten wie μg, Gew%, Vol%, Mol% *etc.* gewählt werden oder vorkommen. Das Klammerzeichen [. . .] wird für Sollgrößen oder durch Ausgleichsrechnung definierte Größen verwendet. Modellanalysen sind nicht nur für eine vorgegebene Menge $[a_1]$ sondern stets für eine Reihe unterschiedlicher Vorgabemengen durchzuführen. Innerhalb des Bereiches der größten und kleinsten Menge liegt der getestete Arbeitsbereich.

Es ist zweckmäßig die Testreihe durch k Gruppen vom Umfang l zu strukturieren, wobei innerhalb der Gruppen gleiche Mengen $[a_1]$ vorgegeben werden. Speziell bei gleichem Gruppenumfang l gilt $n = k \cdot l$. Bei diesem Vorgehen werden die Einzelabweichungen B_1 innerhalb jeder Gruppe häufig zu einem Gruppenmittel $\bar{B}_J$ zusammengefaßt. Die zugehörigen Gruppen-Standardabweichungen s_J oder auch die Variationskoeffizienten VK_J werden sodann als ein Maß für die „Genauigkeit" des Verfahrens angesehen.

Die entsprechenden Rechenvorgänge der k-fachen Gruppenauswertung sind:

Mittelwert	$\bar{B}_J = \dfrac{1}{l} \sum_1^l B_i$	mg	
Standardabweichung	$s_J = \pm \sqrt{\left(\dfrac{1}{l-1} \sum_1^l (B_i - \bar{B}_J)^2 \right)}$	mg	(2)
Variationskoeffizient	$VK_J = \pm 100 \dfrac{s_J}{\bar{B}_J}$	Rel%	

wobei Gruppen-Lauzahl $J = 1, 2, \ldots, k$.

Die ermittelten n Einzelabweichungen B_i bzw. k Gruppenabweichungen $\bar{B}_J$ können durch zufällige Fehler und systematische Fehler bedingt sein. Daß die Resultate a_i systematisch verfälscht sind, wird nur dann erkennbar, wenn für die Abweichungen B_i bzw. $\bar{B}_J$ ein Vorzeichen + (Überbefund) oder — (Unterbefund) stark überwiegt. Über Art und effektive Größe der systematischen Fehler kann man aber bei dieser Auswertungsmethode keine Informationen-erhalten. Eine objektive Beurteilung der Leistungsfähigkeit eines analytischen Verfahrens und eine gezielte Verbesserung der arbeitstechnischen Durchführung setzt jedoch die genaue Kenntnis und damit die Möglichkeit der Ausschaltung oder zumindest rechnerischen Eliminierung systematischer Fehler voraus.

Eventuelle systematische Einflüsse lassen sich mit einer Korrekturgröße $[R]$ für relative systematische Fehler und einer Größe $[U]$ für absolute systematische Fehler fast immer weitgehend erfassen und eliminieren. Im ungünstigsten Fall wird man eine wiedergefundene Menge a_i durch beide Größen korrigieren müssen, wodurch eine korrigierte wiedergefundene Menge a_{Ki} erhalten wird.

$$a_{Ki} = [R](a_i + [U]) \qquad \text{mg} \tag{3}$$

Die gewählte Formulierung (3) hat sachlich analytische Gründe. Ein typisches Beispiel für einen solchen Korrekturausdruck findet man in der Titrimetrie im Zusammenhang des „wahren" Verbrauches V mit dem durch Faktor F und Blindwertverbrauch V_B verfälschtem Rohverbrauch V_x.

$$V = F(V_x - V_B) \qquad \text{ml.}$$

Liegen n nach (3) korrigierte wiedergefundene Mengen a_{Ki} vor, so lassen sich n korrigierte Abweichungen v_i bilden, deren Vorzeichen und numerische Größen praktisch allein vom Zufall abhängen. Eine Zusammenfassung der einzelnen v_i-Werte liefert die Verfahrens-Standardabweichung $[s_K]$, eine einzige Kenngröße der Reproduzierbarkeit, im gesamten Arbeitsbereich.

$$[s_K] = \pm \sqrt{\left(\frac{1}{f}\sum_1^n v_i^2\right)} \qquad \text{mg} \tag{4}$$

mit zufälliger Abweichung $v_i = a_{Ki} - [a_i]$ und Freiheitsgrad f aus Anzahl n der Testanalysen minus der Anzahl 2, 1 oder 0 der erforderlichen Korrekturgrößen.

Bei der nachfolgend beschriebenen Standard-Auswertemethode werden nicht nur die numerischen Werte von $[R]$, $[U]$ und $[s_K]$ sondern auch die mittleren Fehler $[s_R]$ und $[s_U]$ der Korrekturgrößen über eine modifizierte Form der Ausgleichsrechnung ermittelt. Darüber hinaus werden durch mathematisch-statistische Vergleichstests die Realität der Korrekturgrößen $[R]$ und $[U]$ sowie abschließend das gesamte Datenmaterial auf Ausreißer (grobe Fehler) überprüft.

Elektronische Datenverarbeitung

ALGOL (ALGO-rithmic L-anguage) ist eine problemorientierte Programmiersprache mit Vereinbarungen (declarations) und Anweisungen (statements) in englischer Sprache, die relativ leicht erlernbar und vom Typ der bereits sehr zahlreichen elektronischen Datenverarbeitungsanlagen mit ihren speziellen Maschinensprachen unabhängig ist. Ein in ALGOL geschriebenes Programm wird durch ein

vom Maschinentyp abhängiges ALCOR (ALGOL CONVERTER = Übersetzerprogramm) automatisch in die jeweilige Maschinensprache übersetzt und sodann gerechnet. Im allgemeinen steht bei jeder leistungsfähigen Rechenanlage ein ALCOR zur Verfügung.

Die Eingabe eines ALGOL-Programmes in den Rechner erfolgt fast ausschließlich durch Lochstreifen, die von einem Lochstreifen-Lesegerät abgetastet werden. Speziell für ALGOL vorgesehen ist der 5-Spur-Lochstreifen mit dem Codesystem ALCOR CCIT, das bis auf wenige Ausnahmem mit dem internationalen Fernschreibcode CCIT 2 übereinstimmt. Naturgemäß können auch andere Eingabemedien wie etwa der 8-Spur-Lochstreifen oder Lochkarten Verwendung finden, wenn Lesegerät und ALCOR darauf abgestimmt sind.

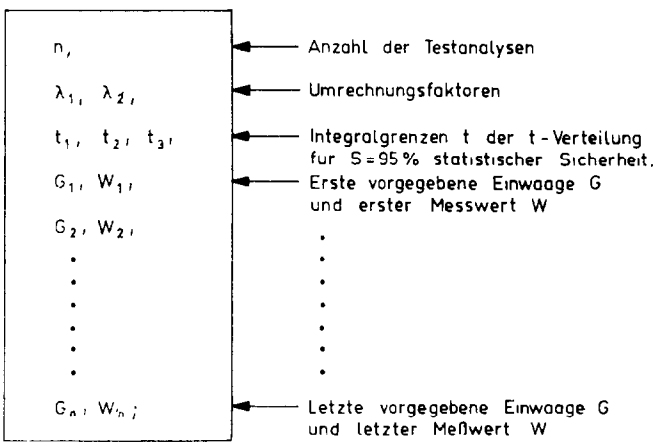

ABB. 1.—Datenliste bei Modellanalysen.

Ein ALGOL-Programm wird nur einmal geschrieben, erprobt und kann sodann in Form des Lochstreifens bei Bedarf immer wieder eingelesen werden. Bei häufiger Verwendung empfiehlt sich die maschineninterne Speicherung direkt als Maschinenprogramm, das durch einen Codenamen abgerufen werden kann. Das hier beschriebene ALGOL-Programm ist erprobt und braucht von einem Benutzer nur sorgfältig abgeschrieben und an ein Rechenzentrum gegeben zu werden. Nach dieser einmaligen Arbeit beschränkt sich seine weitere Tätigkeit auf die Auflistung seiner jeweils ermittelten Untersuchungsbefunde in programmrichtiger Reihenfolge, wie dies Abb 1 zeigt, und die Entgegennahme der Resultate.

Wenn auch für die elektronische Auswertung analytischer Daten bei Vorliegen von Programmen die Kenntnis der Programmiersprache keinesfalls erforderlich ist, so hat es sich doch als sehr vorteilhaft erwiesen, wenn ein oder mehrere Mitarbeiter die im Prinzip sehr einfache ALGOL-Programmierung beherrschen. Es gibt hierzu bereits einige gute Anleitungen, von denen eine Auswahl[1–5] im Literaturteil angeführt ist. Zur Vertiefung sei die Teilnahme an einem ALGOL-Programmierkursus in einem Rechenzentrum empfohlen.

MATHEMATISCHE STRUKTUR

Grunddaten und Ansätze

Bei der Auswertung geht man von der üblichen Minimumbedingung der Ausgleichsrechnung aus, die speziell bei Modellanalysen zu

$$\sum_{1}^{n} v_i^2 = \sum_{1}^{n} (a_{Ki} - [a_i])^2 = \text{MINIMUM} \tag{5}$$

formuliert werden muß. Die korrigierte wiedergefundene Menge wird nicht in jedem Fall durch die Beziehung (3) definiert sein. Es ist durchaus möglich, daß sich die primär errechneten Größen $[R]$ und $[U]$ nicht signifikant von den idealen Sollwerten 1 bzw. 0 unterscheiden. Unter Berücksichtigung aller Möglichkeiten müssen insgesamt 4 verschiedene Korrukturansätze und zugehörige Rechengänge programmiert und gegebenenfalls durchgerechnet werden. Hierzu gibt Tab. I eine Uebersicht.

TABELLE I.—KORREKTURANSÄTZE UND RESULTATE

	Ansatz	Rechengang	f	Resultate
I	$a_{ki} = [R](a_i + [U])$	VOLLKORREKTUR	$n-2$	$[R]$, $[U]$, $[s_k]$, $[s_R]$, $[s_U]$, v_i^*
II	$a_{ki} = a_i + [U]$	ABSOLUTKORREKTUR	$n-1$	$[R] \equiv 1$, $[U]$, $[s_k]$, —, $[s_U]$, v_i^*
III	$a_{ki} = [R] \,.\, a_i$	RELATIVKORREKTUR	$n-1$	$[R]$, $[U] \equiv 0$, $[s_k]$, $[s_R]$, —, v_i^*
IV	$a_{ki} = a_i$	KEINE KORREKTUR	n	$[R] \equiv 1$, $[U] \equiv 0$, $[s_k]$, —, —, v_i^*

v_i^* sind korrigierte Abweichungen $v_i = a_{ki} - [a_i]$, deren numerische Werte größer als ein Streubereich $[s_k] \cdot t$ (95) sind.

Der Minimumansatz (5) kann nach Einsetzen der jeweiligen a_{Ki}-Werte gemäß I, II, III und IV durch partielle Differentiation nach den Konstanten $[R]$ bzw. $[U]$ in einfache Beziehungsgleichungen überführt werden.[6] Die Ausgleichsrechnung muß jedoch stets mit einer Auswertung des Ansatzes I beginnen. Die aus 5 Grundsummen und 3 Determinanten folgenden Primärresultate sind in Tab. II zusammengestellt.

Logische Entscheidungen

Die Realität des Unterschiedes zwischen dem

$[U]$-Wert und dem idealen Sollwert NULL

$[R]$-Wert und dem idealen Sollwert EINS

ist nach dem Sollwert-t-Test[6–8] in einfacher Weise feststellbar. Man formuliert zweckmäßig 2 logische Aussagen (Boole'sche Variable) $V1$ und $V2$, die auf Grund arithmetischer Vergleiche (t-Test) nur „wahr" oder „nicht wahr" sein können.

Mit den Primärresultaten werden gebildet:

$V1$ entspricht „1. Vergleich ist wahr," d.h. „$[U]$ ist real"

$$\text{für} \quad \tau_U = \left| \frac{[U]}{[s_U]} \right| \geqq t_1 \tag{6}$$

V2 entspricht „2. Vergleich ist wahr", d.h. „[*R*] ist real"

$$\text{für} \quad \tau_R = \left| \frac{[R] - 1}{[s_R]} \right| \geqq t_1$$

V1 und *V2* ergeben den logischen Wert „nicht wahr", wenn

$$\left| \frac{[U]}{[s_U]} \right| < t_1 \quad \text{bzw.} \left| \frac{[R] - 1}{[s_R]} \right| < t_1$$

gefunden wird, was den negierten Aussagen „[*U*] ist nicht real" bzw. „[*R*] ist nicht real" entspricht. Mit t_1 sind die Integralgrenzen der *t*-Verteilung für den Freiheitsgrad $f = n - 2$ (2 Konstanten!) und einer Statistischen Sicherheit $S = 95\%$ (Level of Significance 0,05) bezeichnet. Den entsprechenden Wert entnimmt man Tabellen statistischer Zahlenwerte.[6–9] Speziell für $n = 24$ gilt $t_1 = 2{,}074$.

TABELLE II.—GRUNDSUMMEN, DETERMINANTEN, PRIMÄRRESULTATE

Grundsummen
$\mathrm{S1} = \sum_1^n a_1 = \lambda_2 \times \sum_1^n W_1$
$\mathrm{S2} = \sum_1^n a_1^2 = \lambda_2 \times \lambda_2 \times \sum_1^n (W_1 \times W_1)$
$\mathrm{S3} = \sum_1^n [a_1] = \lambda_1 \times \sum_1^n G_1$
$\mathrm{S4} = \sum_1^n [a_1]^2 = \lambda_1 \times \lambda_1 \times \sum_1^n (G_1 \times G_1)$
$\mathrm{S5} = \sum_1^n a_1 \,.\, [a_1] = \lambda_1 \times \lambda_2 \times \sum_1^n (G_1 \times W_1)$
Determinanten
$\mathrm{D} = n \times \mathrm{S2} - \mathrm{S1} \times \mathrm{S1}$
$\mathrm{D}_1 = n \times \mathrm{S5} - \mathrm{S1} \times \mathrm{S3}$
$\mathrm{D}_2 = \mathrm{S2} \times \mathrm{S3} - \mathrm{S1} \times \mathrm{S5}$
Primärrelsultate
$[R] = \frac{\mathrm{D}_1}{\mathrm{D}}$
$[U] = \frac{\mathrm{D}_2}{\mathrm{D}_1}$
$[s_k] = \sqrt{\left(\frac{1}{n-2} \sum_1^n v_1^2\right)} \quad \text{mit} \sum_1^n v_1^2 = \mathrm{S4} - [R] \times (\mathrm{S5} + [U] \times \mathrm{S3})$
$[s_R] = [s_k] \times \sqrt{\left(\frac{n}{\mathrm{D}}\right)}$
$[s_u] = [s_k] \times \sqrt{\left(\frac{\mathrm{S2} + n \times [U] \times [U]}{\mathrm{D}}\right)}$

Die logischen Werte von *V1* und *V2* bestimmen den weiteren Gang der Auswertung. Wenn *V1* UND *V2* „wahr" sind (konjunktive Verknüpfung), so ist nur der Rechengang I (Vollkorrektur) auszuführen und mit der Resultatnotierung abzuschließen. Sind jedoch *V1* ODER *V2* ODER BEIDE „nicht wahr" (disjunktive Verknüpfung), so sind nacheinander die Rechengänge II (Absolutkorrektur) und III (Relativkorrektur) auszuführen. Mit den neuberechneten Werten $[U]$, $[s_U]$ sowie $[R]$, $[s_R]$ müssen analog (6) zunächst neue Aussagen *V1* bzw. *V2* gebildet werden, wobei jedoch t_1 für $f = n - 2$ durch t_2 für $f = n - 1$ (jeweils nur 1 Konstante!) zu ersetzen ist. Speziell für $n = 24$ gilt $t_2 = 2{,}069$.

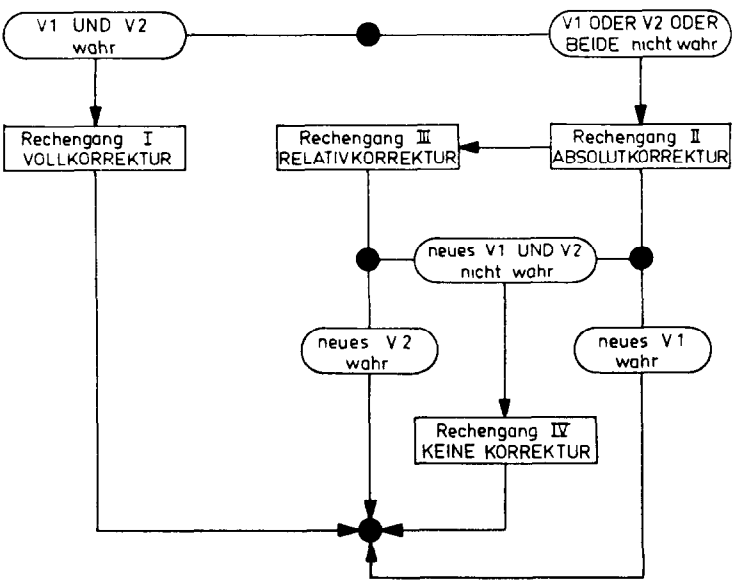

ABB. 2.—Logische Verzweigungen und Rechengänge.

Die Resultate der Rechengänge II oder III sind nur dann von Interesse, wenn *V1* bzw. *V2* als „wahr" gefunden wird. Sind beide Größen „wahr", so resultiert ein Doppelresultat. Welche der Korrekturen sodann praktisch sinnvoll ist, muß extern aus Überlegungen zum chemischen Reaktionsverlauf und zur angewandten Arbeitstechnik entschieden werden. In jedem Fall *V1* ODER *V2* ODER BEIDE „wahr" ist die Auswertung mit der entsprechenden Resultatnotierung abzuschließen.

Der Rechengang III (keine Korrektur) ist nur dann durchzuführen, wenn beide neuen Werte *V1* UND *V2* als „nicht wahr" ermittelt werden. Abb. 2 gibt nochmals einen Überblick der logischen Verzweigungen.

Rechengänge

Der Rechengang I für die Vollkorrektur muß als Basisrechnung in jedem Fall durchgeführt werden. Sofern die logischen Entscheidungen eine Vollkorrektur fordern, sind die Primärresultate nach Tab. II bereits die gesuchten Endergebnisse. Trifft dies nicht zu, so müssen die Rechengänge II und III sowie eventuell auch IV durchgeführt werden, wobei die Resultate aus einer anderen Verknüpfungsform der Grundsummen erhalten werden, wie dies Tab. III zeigt.

TABELLE III.—RESULTATE BEI DEN RECHENGÄNGEN II, III, UND IV

II Absolutkorrektur
$[R] \equiv 1$
$[U] = \frac{1}{n} \times (\mathrm{S3} - \mathrm{S1})$
$[s_k] = \sqrt{\left(\frac{1}{n-1}\sum_1^n v_i^2\right)}$ mit $\sum_1^n v_i^2 = \mathrm{S4} + \mathrm{S2} - 2 \times \mathrm{S5} + n \times [U] \times [U]$
$[s_U] = \frac{[s_k]}{\sqrt{n}}$
III Relativkorrektur
$[U] \equiv 0$
$[R] = \frac{\mathrm{S5}}{\mathrm{S2}}$
$[s_k] = \sqrt{\left(\frac{1}{n-1}\sum_1^n v_i^2\right)}$ mit $\sum_1^n v_i^2 = \mathrm{S4} - [R] \times \mathrm{S5}$
$[s_R] = \frac{[s_k]}{\sqrt{(\mathrm{S2})}}$
IV keine Korrektur
$[R] \equiv 1$ und $[U] \equiv 0$
$[s_k] = \sqrt{\left(\frac{1}{n}\sum_1^n v_i^2\right)}$ mit $\sum_1^n v_i^2 = \mathrm{S4} + \mathrm{S2} - 2 \times \mathrm{S5}$

Prüfung der korrigierten Abweichungen

Die n korrigierten Abweichungen stellen eine vom Rechengang abhängige Wertreihe dar. Bei einwandfreiem Datenmaterial dürfen diese v_i-Werte einen Streubereich $[s_K] \cdot t$ weder beliebig weit noch beliebig oft überschreiten. So sind Überschreitungsabweichungen

$$|v_i^*| \geqq [s_K] \cdot t \qquad \text{bzw.} \qquad \tau = \frac{|v_i^*|}{[s_K]} \geqq t \tag{7}$$

bei t-Werten der Statistischen Sicherheiten

$$\begin{aligned} S = 95\% &: 1 \text{ Mal unter } 20 \quad v_i\text{-Werten} \\ S = 99\% &: 1 \text{ Mal unter } 100 \quad v_i\text{-Werten} \\ S = 99{,}9\% &: 1 \text{ Mal unter } 1000 \quad v_i\text{-Werten} \end{aligned}$$

zu erwarten. Werden z.B. bei $n = 24$ Modellanalysen mehr als 2 v_i-Werte mit $|v_i^*| = [s_K] \cdot t(95)$ oder sogar solche mit $|v_i^*| = [s_K] \cdot t(99)$ bzw. $|v_i^*| = [s_K] \cdot t(99{,}9)$ gefunden, so kann auf „überzufällige" Sondereinflüsse bei den betroffenen Werten geschlossen werden. Die entsprechenden Testanalysen und sodann die gesamten Auswertungsschritte sind zu wiederholen. Erfahrungsgemäß ergibt sich eine solche Notwendigkeit relativ selten.

Im Rahmen des hier angeführten ALGOL-Programmes werden in jedem Rechengang zwar die entsprechenden n Abweichungen v_i berechnet, jedoch die Versuchsnummer i und die Abweichung nur dann ausgegeben, wenn

$$\frac{|v_i^*|}{[s_K]} \geqq t(95)$$

gefunden wird. Der weitere Vergleich ausgegebener v_i^*-Werte mit Streubereichen $[s_K]\cdot t(99)$ und $[s_K]\cdot t(99{,}9)$ hat extern zu erfolgen. Tab. IV gibt eine Zusammenstellung der t-Werte speziell für $n = 24$ Modellanalysen.

TABELLE IV.—t-WERTE BEI $n = 24$ MODELLANALYSEN

Rechengang	f	S = 95%	S = 99%	S = 99,9%
I	22	$t_1 = 2{,}074$	$t_1' = 2{,}819$	$t_1'' = 3{,}792$
II oder III	23	$t_2 = 2{,}069$	$t_2' = 2{,}807$	$t_2'' = 3{,}767$
IV	24	$t_3 = 2{,}064$	$t_3' = 2{,}797$	$t_3'' = 3{,}745$

t_1, t_2, t_3 sind Bestandteile der Datenliste (input).

Die Größe TAU $= \frac{[v_i^*]}{[s_K]}$ wird ausgedruckt und ist direkt mit t, t' oder t'' vergleichbar.

PROGRAMMIERUNG

Flußdiagramm

Abbildung 3 zeigt das vollständige Ablaufschema der Auswertung von Modellanalysen.

Die logischen Entscheidungen treten als Programmverzweigungen in Erscheinung und werden als BEDINGTE Anweisungen formuliert, wobei zwischen alternativer Formulierung

'IF' (Aussage wahr) 'THEN' .... 'ELSE' .... ;

und einseitiger Formulierung

'IF' (Aussage wahr) 'THEN' .... ;

zu unterscheiden ist. Die in abgerundete Tableaus gesetzten Aussagen wirken als „logische Filter" innerhalb der Ablauflinien.

ALGOL-Programm

Das in Tab. V zusammengestellte ALGOL-Programm ist auch ohne ALGOL-Kenntnisse verständlich, wenn man einige Besonderheiten beachtet.

Im ALCOR CCIT-Code sind nur Großbuchstaben (Fernschreib-Schriftbild) oder nur Kleinbuchstaben definiert. Das hier angeführte Programm wurde in Großbuchstaben geschrieben (siehe Zusammenfassung).

Zur Speicherplatz-Reservierung dienen Vereinbarungen (declarations), die alle im Programm verwendeten Variablennamen enthalten müssen. Je nach Variabletyp werden sie in ALGOL durch die Wortsymbole 'REAL' (Gleitkommavariable), 'INTEGER' (Ganzzahlige Variable), 'BOOLEAN' (Aussage-Variable) oder 'ARRAY'

(Variablentabelle) gekennzeichnet. Prozedurvereinbarungen (Unterprogramme) werden mit 'PROCEDURE' eingeleitet.

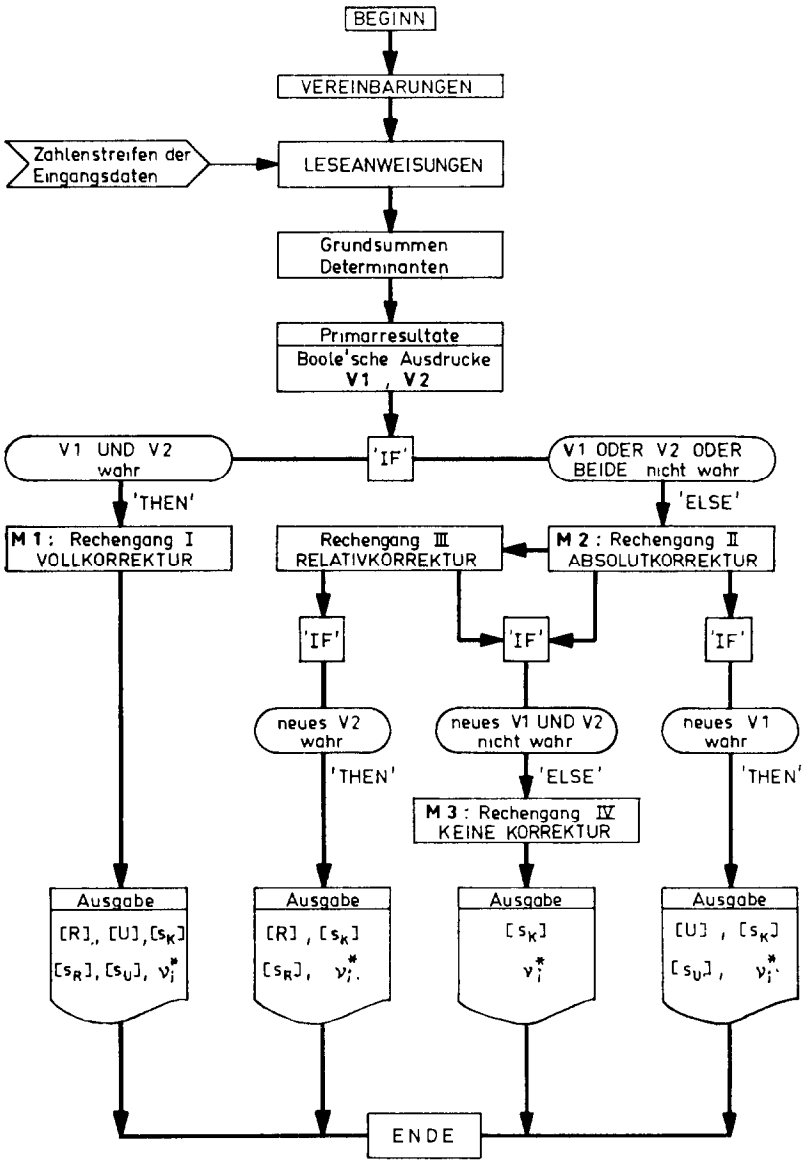

ABB. 3.—Flussdiagramm der Auswertung von Modellanalysen.

Für das arithmetische Vergleichszeichen $\geqq$ (größer und gleich) der Beziehungen (6) und (7) steht in ALGOL das Wortsymbol 'NOT LESS' (nicht kleiner als), während fur die konjunktive logische Verknüpfung von Aussagen 'AND' und für die disjunktive Verknüpfung 'OR' zu setzen ist.

Die Rechengänge werden durch Marken strukturiert und durch eine Folge von Anweisungen (statements) formuliert, wobei neben einfachen arithmetischen oder

TABELLE V.—ALGOL-PROGRAMM FÜR DIE AUSWERTUNG VON MODELLANALYSEN

```
'BEGIN' 'COMMENT' AUSWERTUNG MODELLANALYSEN;
  'REAL' L1, L2, T1, T2, T3, S1, S2, S3, S4, S5, D, R, U, SK, SR, SU, TAU;
  'INTEGER' N, I;
  'BOOLEAN' V1, V2;
  'PROCEDURE' PRUEF (N, U, R, SK, T, WA, VA);
    'REAL' U, R, SK, T;
    'INTEGER' N;
    'ARRAY' WA, VA;

    'BEGIN'
      'REAL' ABW, TAU; 'INTEGER' I;

      'FOR' I: = 1 'STEP' 1 'UNTIL' N 'DO'
        'BEGIN' ABW: = R × (WA[I] + U) − VA[I];
                TAU: = ABS (ABW)/SK;
            'IF' TAU 'NOT LESS' T 'THEN'
            'BEGIN' WRITE ("< ≡ 14 I 7 [A] 15 ABW 15 TAU");
                PRINT (I, VA[I], ABW, TAU); 'END';
      'END' DATENPRUEFUNG;
    'END' PROZEDUR PRUEF;

  READ (N, L1, L2, T1, T2, T3);
  WRITE ("< ≡ MODELLANALYSEN, UMFANG _ N ="); TYPE (N);
  WRITE ("< ≡ 7 T1 15 T2 15T3"); PRINT (T1, T2, T3);

  'BEGIN'
    'ARRAY' G, W, VA, WA [1: N];
    'FOR' I: = 1 'STEP' 1 'UNTIL' N 'DO' READ (G[I], W[I]);
    S1: = S2: = S3: = S4: = S5: = 0;
    'FOR' I: = 1 'STEP' 1 'UNTIL' N 'DO'
      'BEGIN'
        VA[I]: = L1 × G[I]; WA[I] = L2 × W[I];
            S1: = S1 + WA[I] × WA[I];
            S2: = S2 + WA[I];
            S3: = S3 + VA[I];
            S4: = S4 + VA[I] × VA[I];
            S5: = S5 + WA[I] × VA[I];
      'END' SUMMIEREN;
     D: = N × S2 − S1 × S1;
     R: = (N × S5 − S1 × S3)/D;
     U: = (S2 × S3 − S1 × S5)/(R × D);
    SK: = SQRT ((S4 − R × (S5 + U × S3))/(N − 2));
    SR: = SK × SQRT (N/D);
    SU: = SK × SQRT ((S2 + N × U × U)/D)/R;
    TAU: = ABS (U/SU); V1: = TAU 'NOT LESS' T1;
    WRITE ("< ≡ TAU[U] ="); TYPE (TAU);
    TAU: = ABS ((R − 1)/SR); V2: = TAU 'NOT' LESS' T1;
    WRITE ("< ≡ TAU[R] ="); TYPE (TAU);
    'IF' V1 'AND' V2 'THEN' 'GO TO' M1 'ELSE' 'GO TO' M2;
  M1: WRITE ("< ≡ ≡ VOLLKORREKTUR");
    WRITE ("< ≡ 5 [R] 14 [U] 14 [SK] 13 [SR] 13 [SU]");
    PRINT (R, U, SK, SR, SU);
    PRUEF (N, U, R, SK, T1, WA, VA);
    'GO TO' ENDE;
  M2: WRITE ("< = = ABSOLUTKORREKTUR _ [R] = 1");
      U: = (S3 − S1)/N;
     SK: = SQRT ((S4 + S2 − 2 × S5 − N × U × U)/(N − 1));
     SU: = SK/SQRT (N);
    TAU: = ABS (U/SU); V1: = TAU 'NOT LESS' T2;
    WRITE ("< ≡ TAU[U] ="); TYPE (TAU);
```

(TABELLE V. *Contd.*)

```
'IF' V1 'THEN'
  'BEGIN' WRITE ("< ≡ ␣5 [U] ␣14 [SK] ␣13 [SU]"); PRINT (U, SK, SU);
      PRUEF (N, U, 1, SK, T2, WA, VA);
    'END' AUSGABE 'ELSE'
  WRITE ("< ≡ UNTERSCHIED ␣ VON ␣ [U] ␣ ZU ␣ NULL ␣ NICHT ␣ FEST-
    STELLBAR");

  WRITE ("< ≡ ≡ RELATIVKORREKTUR ␣ [U] = 0");
    R: = S5/S2;
  SK: = SQRT ((S4 − R × S5)/(N − 1));
  SR: = SK/SQRT (S2);
  TAU: = ABS ((R − 1)/SR); V2: = TAU 'NOT LESS' T2;
  WRITE ("< ≡ TAU[R] ="); TYPE (TAU);

  'IF' V2 'THEN'
    'BEGIN' WRITE ("< ≡ ␣5 [R] ␣14 [SK] ␣13 [SR]"); PRINT (R, SK, SR);
        PRUEF (N, 0, R, SK, T2, WA, VA);
    'END' AUSGABE 'ELSE'
  WRITE ("< ≡ UNTERSCHIED ␣ VON ␣ [R] ␣ ZU ␣ EINS ␣ NICHT ␣ FEST-
    STELLBAR");

  'IF' V1 'OR' V2 'THEN' 'GO TO' ENDE 'ELSE' 'GO TO' M3;

M3: WRITE ("< ≡ ≡ KEINE ␣ KORREKTUR ␣ [R] = 1, [U] = 0");
  SK: = SQRT ((S4 + S2 − 2 × S5)/N);
  WRITE ("< ≡ [SK] ="); TYPE (SK);
  PRUEF (N, 0, 1, SK, T3, WA, VA);

'END' FELDVEREINBARUNGEN;

ENDE: 'END' PROGRAMM FUER MODELLANALYSEN
```

logischen Ausdrücken (expression statements) Laufanweisungen (for statements), Sprunganweisungen (go to statements) und bedingte Anweisungen (if statements) zu unterscheiden sind.

Der Dateneingabe dient die Leseanweisung READ und der Datenausgabe die Anweisungen PRINT, WRITE und TYPE. In neueren ALCORS[5] werden diese 4 Anweisungen durch differenziertere Prozeduren ersetzt, jedoch ist hier die Entwicklung noch keineswegs abgeschlossen. Die Betriebszeichen eines ALGOL-Schreibers

Wagenrücklauf WR, Symbol <

Zeilenvorschub ZV, Symbol ≡

Zwischenraum ZW, Symbol ␣

sind im allgemeinen ohne Einfluß auf den Programmablauf. Im Rahmen einer Ausgabeanweisung WRITE ("Zeichenkette") sind sie aber zu beachten und für das Ausgabebild von Bedeutung. Im vorliegenden Programmbild sind diese Zeichen in den Zeichenketten der WRITE-Anweisungen ausdrücklich angeführt, wobei mehrfache Zwischenräume, z.B. 12 mal ␣, durch ␣12 gekennzeichnet werden.

Hinsichtlich weiterer Einzelheiten zur ALGOL-Programmierung sei auf die angeführte Literatur[1–5] verwiesen.

BEISPIELE

Nachfolgende Beispiele wurden an einer relativ kleinen und langsamen Rechenanlage ZUSE Z23 gerechnet. Der Zeitbedarf für das einmalige Einlesen des

ALGOL-Programmes beträgt 4½ Minuten. Für das Einlesen des Zahlenstreifens der Eingangsdaten sowie für Rechnung und Resultatausgabe werden je Beispiel weitere 1½ Minuten benötigt, so daß die Auswertung beider Beispiele in weniger als 8 Minuten beendet ist. Bei 1 Std Rechenzeit können mehr als 30 derartiger Modellanalysenreihen ausgewertet werden, die bei konventioneller Rechentechnik mehr als 1 Monat Arbeitszeit pro Person beanspruchen würden.

Titrimetrische Chloridbestimmung nach Mohr

Makro-Arbeitsbereich: 1,0 bis 0,05 mMol Chlorid, entsprechend 35 bis 1,8 mg Chlorid.

Modellanalysen: $k = 6$ Testgruppen mit jeweils $l = 4$ Einwaagen G_i an Standardlösung von etwa 10/7,5/5,0/2,5/1,0/0,5 Gramm, entsprechend etwa 1,0/0,75/0,50/0,25/0,10/0,5 mMol Chlorid.

Bürette: 10 ml-Normalbürette, Teilung 0,02 ml oder Kolbenbürette, Teilung 0,005 ml: Tropfengröße unter 0,03 ml.

Standardlösung: Wässerige Natriumchloridlösung (etwa 0,1M) mit $\lambda_1 = 3{,}5472$ mg Cl/Gramm Lösung; $[a_i] = \lambda_1 G_i$ mg Cl/Einwaage.

Kurzvorschrift: Maximal 50 ml mit 0,5*M* $NaHCO_3$ neutralisierte Probelösung (pH 7–8) in 300 ml Weithals-Erlenmeyerkolben +1,0 ml 0,5*M* Kaliumchromat + 50 ml Äthanol + Wasser bis Endvolumen von 100 ml. Sofort Titration mit 0,1*N* Silbernitrat-Maßlösung bis zum scharfen Umschlag von Hellgelb nach Rotbraum. Rohverbrauch V_x ml (Bereich 10 bis 0,5 ml).

Blindwerte und Faktor: 10 Blindansätze mit den verwendeten Reagentien ergaben im Mittel: $\bar{V}_B = 0{,}026$ ml; $s_B = \pm 0{,}005_3$ ml. Faktor F der Maßlösung: $F = 1{,}000$ (Herstellergarantie ±0,2 Rel%).

Titrationsergebnis: $W_i = V_i = F(V_{xi} - \bar{V}_B) = V_{xi} - 0{,}026$ ml. Die Meßgröße W_i wird extern berechnet. In Fällen $F \neq 1{,}000$ kann F in den Umrechnungsfaktor einbezogen werden. Gefundene Menge: $a_i = \lambda_2 . V_i$ mg Chlorid mit $\lambda_2 = [\mathrm{Cl}] . N$ (bzw. $F . [\mathrm{Cl}] . N$) = 3,5453 mg Cl/ml Verbrauch.

Tabelle VI gibt eine Zusammenstellung der Eingangsdaten in programmrichtiger Reihfolge,

TABELLE VI.—INPUT/OUTPUT—DATEN DER TITRIMETRISCHEN CHLORIDBESTIMMUNG

Datenauflistung der Versuchsergebnisse (input)

```
24,
 3·5472,  3·5453,
 2·074,   2·069,   2·064,
 9·9686,  9·944,   9·9035,  9·924,  9·8176,  9·824,  9·9784,  9·964,
 7·4581,  7·494,   7·5330,  7·574,  7·4427,  7·474,  7·4585,  7·534,
 4·9815,  4·994,   5·0723,  5·064,  5·0157,  5·004,  5·0854,  5·074,
 2·5546,  2·564,   2·6228,  2·644,  2·6255,  2·614,  2·5110,  2·524,
 1·1017,  1·084,   1·0507,  1·034,  1·1762,  1·154,  1·1403,  1·114,
 0·5373,  0·514,   0·5468,  0·534,  0·5739,  0·554,  0·5592,  0·534;
```

Ausgedruckte Resultate (output)

```
ALCORA ZUSE Z 23 MODUS 4
MODELLANALYSEN, UMFANG  N = 24
      T1                T2                T3
0·207400000₁₀1    0·206899999₁₀1    0·206400000₁₀1
TAU[U] = 0·196646322₁₀1
TAU[R] = 0·223333112₁₀1

ABSOLUTKORREKTUR [R] = 1
TAU[U] = 0·294087212
UNTERSCHIED VON [U] ZU NULL NICHT FESTSTELLBAR

RELATIVKORREKTUR [U] = 0
TAU[R] = 0·104251136₁₀1
UNTERSCHIED VON [R] ZU EINS NICHT FESTSTELLBAR

KEINE KORREKTUR [R] = 1, [U] = 0
[SK] = 0·880712841₁₀−1
   I        [A]              ABW              TAU
   8   0·264567912₁₀2    0·253498999    0·287833887₁₀1
```

wobei die Wertepaare G_i, V_i nach den 6 Gruppen geordnet sind, sowie das Originalbild der von der Rechenanlage ausgedruckten Resultate und Urteile.

Diskussion. Nach Auflistung der statistischen Vergleichsgrößen t_1, t_2 und t_3 werden die nach Beziehung (6) mit den Primärresultaten gebildeten Prüfgrößen τ_U und τ_R ausgegeben. Wegen $\tau_U = 1{,}967 < t_1 = 2{,}074$ d.h. „*V1* nicht wahr", und $\tau_R = 2{,}233 > t_1 = 2{,}074$ d.h. „*V2* wahr", wird die Marke M2 des Programmes angesteuert und $[U]$ bzw. $[R]$ in den Einzelrechengängen II und III erneut berechnet.

Da hierbei $\tau_U = 0{,}294 < t_2 = 2{,}069$ d.h. „neues *V1* nicht wahr", und auch $\tau_R = 1{,}043 < t_2 = 2{,}069$ d.h. „neues *V2* nicht wahr" resultiert, wird das Programm nach Ausdrucken der Urteile

UNTERSCHIED VON $[U]$ ZU NULL NICHT FESTSTELLBAR
UNTERSCHIED VON $[R]$ ZU EINS NICHT FESTSTELLBAR

bei der Marke M3 fortgesetzt. Der Rechengang IV liefert als Endresultat die Verfahrens-Standardabweichung $[s_K] = \pm 0{,}0881$ mg Chlorid entsprechend $s_V = [s_K]/\lambda_2 = \pm 0{,}025$ ml Maßlösung. Der Befund $[U] = 0$ und $[R] = 1$ beweist, daß die übliche Korrektur von Titrationsergebnissen durch gesondert ermittelte Blindwerte V_B und Faktoren F bei dem vorliegenden Verfahren ausreichend und einwandfrei ist.

Modellanalyse Nr. 8 mit $[a_1] = 26{,}46$ mg Chlorid ergab einen „überzufälligen", Abweichungswert von $v_1^* = +0{,}253$ mg Chlorid (Überbefund). Wegen $\tau = 2{,}878 > t_3' = 2{,}792$ ($S = 99\%$!) liegt der relativ seltene Fall einer „unzulässigen" Überschreitung des Streubereiches vor und die betreffende Modellanalyse wurde wiederholt, wobei $G_8 = 7{,}4817$ g, d.h. $[a_8] = 26{,}54$ mg Chlorid; $W_8 = 7{,}524$ ml, d.h. $a_8 = 26{,}68$ mg Chlorid gefunden wurde. Eine erneute Durchrechnung ergab hinsichtlich $[U]$ und $[R]$ gleiche Urteile, jedoch im Rechengang IV eine kleinere Standardabweichung von $[s_K] = \pm 0{,}0773$ mg Chlorid entsprechend $s_V = \pm 0{,}022$ ml Maßlösung.

Gravimetrische Wolframbestimmung mit 8-Oxychinolin

Makro-Arbeitsbereich:	1,0 bis 0,1 mMol Wolfram entspricht 184 bis 18,4 mg Wolfram.
Modellanalysen:	$k = 6$ Testgruppen mit jeweils $l = 4$ Einwaagen G_i an Standardlösung von etwa 10/8/6/2/1 Gramm entsprechend etwa 1,0/0,8/0,6/0,4/0,2/0,1 mMol Wolfram.
Geräte:	Fällungsregler-Kombination, Filtertiegel Schott u. Gen. 63aG4, Saugtopf u.a.m.
Standardlösung:	Natriumwolframat in 0,2*M* Natriumhydroxid (etwa 0,1*M* an Wolfram mit $\lambda_1 = 18{,}385$ mg Wolfram/Gramm Lösung; $[a_i] = \lambda_1 \cdot G_i$ mg Wolfram.
Kurzvorschrift:	Maximal 170 ml Probelösung mit höchstens 2 mMol freier Natriumhydroxid in 400 ml-Becherglas (hohe Form) + 25,0 ml 0,5*M* Oxalsäure + 10,0 ml 0,25*M* ÄDTA + 5,0 ml 2*M* Ammoniak + Wasser auf 200–210 ml, pH 2,5 ± 0,5. Unter Rühren auf 70–80° erwärmen, Lösung klar, +30,0 ml 0,1*M* Oxinlösung (1*M* an Essigsäure) schnell unter Rühren eintropfen, 5 min Rühren, dann +15,0 ml 2*M* Ammoniak innerhalb von 20–25 min aus Fällungsregler unter Rühren eintropfen. Temperatur der Lösung auf 70–80° halten. Fällung 30 min bei 70–80°C ausrühren. End-pH 5,0 ± 0,5. Noch warm über Tiegel 63aG4 filtrieren. Filtrat auffangen und mit 50° heißem Filtrat letzte Niederschlagsreste aufbringen. Nachwaschen durch Auftropfen von insgesamt 25 ml Wasser (70° warm). Bei 160°C zunächst 60 min, danach in Intervallen von 30 min konstant trocknen. (Gewichtskonstanz auf ±0,05 mg). Wägeform: $WO_2(Ox)_2$, M = 504,157. Auswaage: $A_x$mg (Bereich 500–50 mg).
Blindwerte:	4 Blindansätze mit den verwendeten Reagentien ergaben keine sichtbaren und wägbaren Fällungen, d.h. $A_B = 0{,}00$ mg.
Fällungsergebnis:	Gefundene Menge $a_i = \lambda_2 \cdot A_{xi}$ mg Wolfram mit $\lambda_2 = [W]/[WO_2(Ox)_2] = 0{,}36467$ mg W/mg Auswaage.

TABELLE VII.—INPUT/OUTPUT—DATEN DER GRAVIMETRISCHEN WOLFRAMBESTIMMUNG

Datenauflistung der Versuchsergebnisse (input)

```
24,
18·385,     0·36467,
 2·074,      2·069,      2·064,
10·1640,   511·09,     10·1808,   512·48,   10·0339,   505·69,   10·0243,   504·57,
 8·2520,   417·13,      8·2292,   415·78,    8·0841,   408·45,    8·0746,   406·98,
 5·9243,   299·73,      6·0203,   304·25,    5·9696,   302·31,    6·0927,   308·69,
 3·9912,   202·19,      4·1406,   209·58,    4·0587,   205·36,    3·9871,   201·58,
 1·9942,   101·05,      1·9919,   101·45,    2·0322,   103·29,    2·0105,   102·08,
 1·0211,    51·63,      1·0340,    52·18,    1·0258,    52·07,    1·0394,    53·08;
```

Ausgedruckte Resultate (output)

```
ALCORA ZUSE Z23 MODUS 4

MODELLANALYSEN, UMFANG   N = 24
  T1              T2              T3
0·207400000₁₀1  0·206899999₁₀1  0·206400000₁₀1
TAU[U] = 0·368230876₁₀1
TAU[R] = 0·209101715₁₀1
VOLLKORREKTUR
    [R]             [U]            [SK]           [SR]            [SU]
0·100174262₁₀1  −0·346040237  0·241556638  0·833387456₁₀−3  0·939737160₁₀−1
     I          [A]            ABW            TAU
     1  0·186865140₁₀3  −0·507803200  0·210221174₁₀1
```

Tabelle VII gibt eine Zusammenstellung der Eingangsdaten in programmrichtiger Reihenfolge, wobei die Wertepaare G_i, A_i nach den 6 Gruppen geordnet sind, sowie das Originalbild der von der Rechenanlage ausgedruckten Resultate und Urteile.

Diskussion. Nach Auflistung der statistischen Vergleichsgrößen t_1, t_2 und t_3 werden die nach Beziehung (6) mit den Primärresultaten gebildeten Prüfgrößen τ_U und τ_R ausgegeben.

Wegen $\tau_U = 3{,}682 > t_1 = 2{,}074$ d.h. „*V1* wahr" und $\tau_R = 2{,}091 > t_1 = 2{,}074$ d.h. „*V2* wahr", wird die Marke M1 angesteuert. Die bereits berechneten Primärresultate

$$[R] = 1{,}00174$$

$$[U] = -0{,}346 \text{ mg W}$$

$$[s_K] = \pm 0{,}242 \text{ mg W}$$

$$[s_R] = \pm 0{,}00083$$

$$[s_U] = \pm 0{,}094 \text{ mg W}$$

werden für dieses Verfahren als maßgebende Korrekturgrößen ausgegeben. Das negative $[U]$ ist wegen $\tau_U > t_1' = 2{,}819$ ($S = 99\,\%$!) signifikant Kleiner als Null und korrigiert einen Überbefund durch Mitreißen von Verunreinigungen bei Fällungen von Wolframmengen an der unteren Grenze des Arbeitsbereiches. Wegen $\tau_R < t_1'$ ist $[R]$ nur wahrscheinlich größer als 1. $[R]$ korrigiert Unterbefunde durch Löslichkeit bei Fällungen von Wolframmengen der oberen Grenze des Arbeitsbereiches.

Das Verfahren ist in dieser Form keinesfalls optimal und es wurden weitere gezielte Untersuchungen zur Ausschaltung der systematischen Fehlerquellen durchgeführt, worauf hier jedoch nicht eingegangen werden kann.

Modellanalyse Nr. 1 ergab einen Abweichungswert $v_1^* = -0{,}508$ mg Wolfram (Unterbefund) der wegen $\tau = 2{,}102 < t_1 = 2{,}819$ jedoch zulässig ist.

Résumé—La méthode usuelle d'évaluation d'une méthode analytique consiste à mener une série d'expériences-types. Une comparaison entre la quantité prélevée et la quantité trouvée donne une information numérique objective sur le hasard et les erreurs systématiques dans le domaine particulier étudié. Si l'on utilise les méthodes ordinaires de calcul, le temps nécessité et les difficultés sont relativement importants. Une série de 24 essais peut nécessiter 8 h pour les calculs, même s'il n'y a pas d'erreur humaine dans les estimations. L'expérience montre que des opérateurs inexpérimentés peuvent avoir besoin de plusieurs jours pour les calculs. On peut obtenir des résultats exempts d'erreur en 5 mn seulement par calcul électronique. On présente un programme de calcul écrit dans le language logique universel ALGOL. Les opérations préparatoires sont si simples qu'une assistance technique n'est pas nécessaire.

Summary—The usual way of evaluating an analytical method is to carry out a series of model experiments. A comparison of the amount taken and the amount found gives objective numerical information about the random and systematic errors in the particular range studied. If conventional methods of calculation are used, the time needed and the difficulty are relatively large. A series of 24 tests may need 8 hr for the calculations, even if no human error in computation occurs. Experience shows that inexperienced operators may need several days for the calculations. Results free from error can be obtained in as little as 5 min by electronic computing. A calculation programme written in the universal logical language ALGOL is given. The preparatory operations are so simple that skilled assistance is not necessary.

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THERMAL STANDARDS IN THERMOGRAVIMETRY

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Summary—Comparisons of thermogravimetric data from different instruments have often led to controversy because of lack of appreciation that the values are influenced by the apparatus used. Consequently, it is suggested that various compounds be employed as thermal standards for comparing data from different sources. The paper also discusses the variables to be considered when attempting to devise such standards and includes a list of suggested thermal standards covering the ranges 100–400° and 1050–1060°.

THE rapid development of thermogravimetry in recent years has meant that there is now a considerable variety of apparatus in use in many different fields of study. This equipment, whether constructed in the laboratory or available commercially, naturally varies considerably in design and performance. Comparisons of so-called decomposition temperatures and other data derived from thermogravimetric curves, have often led to controversy because of lack of appreciation that these values partly depend on the apparatus used.[1] Duval,[2] for example, states that he has been unable to find any compound which gives the same decomposition temperature on five commercial thermobalances of different makes, even though all of the heating conditions were apparently identical.

In an attempt to avoid such controversy, it is suggested that various compounds possessing suitable thermal characteristics be employed as thermal standards. This would mean that if a worker studying the thermal behaviour of a compound in a particular apparatus under a specified set of operating conditions, quotes a certain temperature as being of some consequence, this temperature would be qualified by referring it to a significant temperature on the thermogravimetric curve of a thermal standard, run under identical operating conditions. Ideally, this standard temperature should be close to the significant temperature of the compound under investigation.

Although no extensive study of suitable compounds has been previously published, the idea of thermal standards is not new and probably the substance most studied in this context is calcium oxalate monohydrate. Duval[3] used this material when adjusting thermobalances after they had been assembled, cleaned or repaired and Barcia–Goyanes[4] and Wilson[5] suggested that the extremities of the plateaux of its thermogravimetric curve be used as temperature calibration points for a thermobalance. Such use of the two extremities of the plateaux of any thermogravimetric curve is inadvisable as their position is not dependent solely on the sample.[6,7] However, Simons and Newkirk[7] have shown that if calcium oxalate monohydrate is heated in a thermobalance under carefully controlled conditions, the resultant thermogravimetric curve can be useful in assessing the performance of the thermobalance and in the interpretation of thermogravimetric measurements.

Early in 1965, Forsyth[8] suggested the use of calcium and iron(II) oxalates as

standards for the calibration of thermoanalytical equipment and subsequently[9] enlarged on this idea by using the peak temperatures of the derivative thermogravimetric curve of calcium oxalate monohydrate as calibration points.

It is intended that thermal standards should only be used to avoid controversy when differences (>25°) in critical temperatures are reported by different workers.

EXPERIMENTAL

Decomposition temperature

It is important to realise that in thermogravimetry the term "decomposition temperature" is a misnomer. Although a particular temperature may be the lowest temperature at which the start of a weight change can be observed with a certain apparatus under a given set of experimental conditions, it is not the absolute decomposition temperature below which the reaction rate suddenly becomes zero.[10]

In a thermogravimetric curve of a single stage non-isothermal reaction, there are two characteristic temperatures;[7] the initial temperature, T_i and the final temperature, T_f; T_i is defined as the lowest temperature at which the cumulative weight change reaches a magnitude that a particular thermobalance can detect, and T_f as the temperature at which the cumulative weight change first reaches its maximum value. Although T_i has no fundamental significance, it can still be a useful characteristic of a thermogravimetric curve[6] and the term "procedural decomposition temperature" has been suggested for it.[6,11]

The peak temperature of a derivative thermogravimetric curve is, again, not the decomposition temperature, a fact which has not been appreciated by some workers.[12] Although Forsyth[9] chose this temperature as his reference point, it is not necessarily the ideal point, as McAdie[13] pointed out in connexion with his attempt to establish standard materials for differential thermal analysis.

In this paper, the procedural decomposition temperature, T_i, is the parameter considered in investigation of materials suitable as thermal standards.

Materials studied

In choosing compounds as potential thermal standards it was thought desirable to use materials that were both universally and commercially available in a known state of purity. Accordingly, only chemicals conforming to the AnalaR specification were employed.

Operating details

Thermobalance. A Stanton thermobalance, Model HT-SM, was used for establishing all the reference temperatures given, except the temperatures below 100° quoted for copper(II) sulphate pentahydrate. In this instance, a modified recording system was used (see *Comments on Table II*). The thermobalance used has a sensitivity of 1 mg for each small division of the weight record chart and the sample weights were chosen accordingly (see below). A chart speed of 6 in/hr was chosen to obtain satisfactory resolution of the thermogravimetric curve. All temperatures quoted are furnace wall temperatures.

Sample container. The geometry and the material of manufacture of the sample container will profoundly affect the shape of the thermogravimetric curve.[1,14,15] A shallow platinum dish, 20 mm in diameter and 6 mm deep, was chosen for this study because this design facilitates gaseous exchange between the sample and the surrounding atmosphere.[1,15–18] Platinum was chosen because of its good thermal conductivity and lack of any known catalytic effect on the thermal decomposition of the materials studied.

Sample weight. The weight of sample chosen always gave only a thin layer at the bottom of the platinum dish. This allowed free diffusion of the gaseous products through the void space round the particles and made any temperature gradient in the sample negligible in comparison with the temperature differences being investigated. At the same time, the sample weight was sufficient to give an adequate weight change, relative to the sensitivity of the thermobalance.

State of sub-division of the sample. The effects of particle size and surface area have been widely studied[7,19–23] although it has been shown[24] that although the final temperature T_f and the rate of weight loss vary markedly with particle size, the procedural decomposition temperature T_i is not affected. In the present work, all samples with the exception of calcium carbonate (which was obtainable in analytical reagent grade only in a very finely divided form) were lightly ground so that all the material passed a No. 100 British Standard sieve. The fraction passing a No. 100 and retained on a No. 200 British Standard sieve was then used in the experiments.

Heating rate. That the heating rate can markedly influence the overall shape of a thermogravimetric curve was stressed by early workers[19,20] and the effect has subsequently been studied in a variety of applications.[21,23,25,26,27] Newkirk[6] has shown that at a given temperature the degree of decomposition is greater, the slower the heating rate. Further, the appearance of an inflexion in a thermogravimetric curve at a fast heating rate may resolve into a plateau at a slower heating rate.[28] There is therefore neither an optimum nor a standard heating rate, but in the light of past experience[27] and of other workers' results[1,6,28] a heating rate of 3°/min was considered suitable.

Gas atmosphere. The effect of the atmosphere present has also been studied and it has been found that it can be considerable.[1,7,29,30] Clearly there is no gas atmosphere suitable for all cases, and any choice is open to question. A static air atmosphere was chosen for the current investigation with a full appreciation of its possible shortcomings.

RESULTS

Since it had been decided to use the procedural decomposition temperature T_1 as the reference temperature, a variety of compounds was run on the thermobalance in order to obtain some preliminary information. Table I summarizes the results obtained. From a study of the Table and the corresponding thermogravimetric curves, it was apparent that in order to determine T_1 unambiguously, the initial rate of weight loss as recorded on the Stanton thermobalance should be not less than $2\frac{1}{2}$ mg/5 min. Appropriate compounds from Table I were selected for further study. To be suitable as a standard of this type, any potential standard compound should

(i) be stable at room temperature for at least 12 months,
(ii) give reproducibility of reference temperatures to $\pm 5°$,
(iii) give agreement between operators to $\pm 5°$ for the value of the reference temperature,
(iv) give agreement to $\pm 15°$ for different batches from the same supplier, and
(v) give reference temperatures differing by not more than 25° for samples from different suppliers.

The first requirement was satisfied because the work took about 18 months and the thermogravimetric curves of the compounds suggested as thermal standards varied little during this time. The other four requirements were covered by using samples from two different supply houses, one of which provided samples from different batches, and by having separate thermogravimetric runs carried out by two operators and the suggested reference temperatures, in almost every case, read off the same thermogravimetric curves by both operators. The results obtained are summarized in Table II.

Comments on Table II

With the exception of that for copper(II) sulphate pentahydrate, the reference temperatures below 100° are only approximate values and have been included merely as an indication of compounds which may be suitable as standards at low temperatures The suggested reference temperatures of 52–3° and 86° for copper(II) sulphate pentahydrate were obtained with a modified Stanton thermobalance which instead of recording temperature, recorded the voltage of a chromel/alumel thermocouple over the range 0–22 mV (0–530°). The overall results indicate good reproducibility of the reference temperatures and satisfactory agreement between operators. Most of the compounds gave satisfactory agreement between samples from different sources and different batches, the exceptions being sucrose, barium acetate, potassium hydrogen phthalate and sodium hydrogen tartrate.

TABLE I.—COMPOUNDS STUDIED FOR POSSIBLE USE AS THERMAL STANDARDS

Compound	Weight used *mg*	Reference temperature °C	Rate of weight loss* *mg/min*
Aluminium ammonium sulphate-24-water	97·9	~50	0·5
Aluminium potassium sulphate-24-water	88·8	~50	1.2
		685	0·4
Ammonium dihydrogen phosphate	98·3	185	0·5
Diammonium hydrogen phosphate	71·6	—	—
Barium acetate	82·4	450	2·8
Barium hydroxide-8-water	105·7	~50	0·8
		100	0·4
Boric acid	90·4	100	1·1
Cadmium acetate dihydrate	86·5	~60	1·0
		250	2·8
Calcium carbonate (−300 mesh)	168·2	—	—
Citric acid	89·3	—	—
Copper(II) acetate monohydrate	131·0	120	0·9
		1055	1·0†
Copper(II) sulphate pentahydrate	132·3	52	0·6
		86	3·0
		220	0·8
		1055	0·8
Magnesium acetate tetrahydrate	151·3	~60	0·4
		320	6·0
Oxalic acid dihydrate	46·6	~50	0·5
		115	0·5
Potassium hydrogen phthalate	135·9	240	0·4
		365	0·4
		565	0·9
Potassium hydrogen tartrate	84·7	240	5·0
Potassium oxalate monohydrate	95·9	~90	1·0
		515	0·3
Potassium tetroxalate dihydrate	91·7	~80	0·8
Potassium titanium oxalate dihydrate	108·6	—	—
Sodium hydrogen tartrate monohydrate	122·3	~75	1·1
		230	>6·0
		545	1·3
Sodium oxalate	131·1	—	—
Succinic acid	74·5	—	—
Sucrose	88·9	210	1·4
Tartaric acid	91·0	185	0·9
Zinc acetate dihydrate	147·1	~50	0·5
Zinc sulphate heptahydrate	141·4	~50	0·5
		225	0·9

* Initial value, averaged over 5 min immediately after procedural decomposition temperature, T_i.
† Averaged over 2½ min.

Some sucrose samples exhibit a small slow weight loss starting at about 170° but this does not interfere with the sharp increase in the rate of weight loss at 205–210°. Barium acetate gives reference temperatures which show good agreement between operators, but the variation of 40° between samples from the same supply house is not acceptable. Potassium hydrogen phthalate shows good agreement for reference temperatures of 240–250° and 365–370°, but one sample gave a further reference temperature of 565° whereas a sample from a different supply house gave an additional reference temperature of 670°. These temperatures are undoubtedly derived from the decomposition of dipotassium phthalate[31] but no explanation can be offered for their

TABLE II.—SUGGESTED THERMAL STANDARDS

Compound	Operator	Reference temperature, °C		
		Supplier A	Supplier B	
			Batch 1	Batch 2
Aluminium ammonium sulphate-24-water	X	~50		
	Y	~50		
Aluminium potassium sulphate-24-water	X	~50		
	Y	~50		
Barium hydroxide-8-water	X	~50		
	Y	~50		
Oxalic acid dihydrate	X	~50		
	Y	~50		
Zinc acetate dihydrate	X	~50		
	Y	~50		
Zinc sulphate heptahydrate	X	~50		
	Y	~50		
Copper(II) sulphate pentahydrate	X	52		
	Y	53		
Cadmium acetate dihydrate	X	~60		
	Y	~60		
Magnesium acetate tetrahydrate	X	~60		
	Y	~60		
Copper(II) sulphate pentahydrate	X	86		
	Y	86		
Potassium tetroxalate dihydrate	X	~80		
	Y		~80	~80
Potassium oxalate monohydrate	X	~90		
	Y	~90		
Boric acid	X	100	100	100
	Y	100	100	100
Oxalic acid	X	115	120	120
	Y	115	120	120
Copper(II) acetate monohydrate	X	120	120	120
	Y	120	120	120
Ammonium dihydrogen phosphate	X	185	190	185
	Y	190	190	185
Tartaric acid	X	185	180	180
	Y	185	180	180
Sucrose	Y	210	205	200
	Y	210	205	200
Copper(II) sulphate pentahydrate	X	220	235	240
	Y	220	230	240
Zinc sulphate heptahydrate	X	225	250	250
	Y	225	245	250
Sodium hydrogen tartrate monohydrate	X	230	240	240
	Y	230	240	240
Potassium hydrogen phthalate	X	240	250	
	Y	240	250	
Potassium hydrogen tartrate	X	240	260	260
	Y	245	255	260
Cadmium acetate dihydrate	X	250	250	250
	Y	250	250	250
Magnesium acetate tetrahydrate	X	320	320	315
	Y	320	320	320
Potassium hydrogen phthalate	X	365	370	
	Y	365	370	
Barium acetate	X	450	440	400
	Y	450	440	400

TABLE II.—(*Contd.*)

Compound	Operator	Reference temperature, °C		
		Supplier A	Supplier B	
			Batch 1	Batch 2
Sodium hydrogen tartrate monohydrate	X	545	545	no weight loss
	Y	545	545	
Potassium hydrogen phthalate	X	565	670	
	Y	565	670	
Copper(II) acetate monohydrate	X	1055	1060	1055
	Y	1055	1060	1060
Copper(II) sulphate pentahydrate	X	1055	1050	1055
	Y	1055	1050	1050

wide divergence. They cannot, of course, be recommended as reference temperatures. Sodium hydrogen tartrate gives a useful reference temperature of 545° but, as will be seen from Table II, although this temperature is reproducible with samples from different supply houses, it is not given by all samples. Consequently its use as a thermal standard must be treated with some reserve.

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Zusammenfassung—Der Vergleich thermogravimetrischer Daten von verschiedenen Geräten führte oft zu Diskussionen, da der Einfluß des Geräts außer Acht gelassen wurde. Daher wird vorgeschlagen, daß verschiedene Verbindungen als thermische Standards zum Vergleich der Daten von verschiedenen Geräten herangezogen werden. Die Arbeit diskutiert auch die Variablen, die bei einem Versuch, solche Standards aufzustellen, berücksichtigt werden müssen, und enthält eine Liste vorgeschlagener thermischer Standards in den Bereichen 100–400° und 1050–1060°.

Résumé—Des comparaisons de données thermogravimétriques obtenues avec différents instruments ont souvent conduit à des controverses parce qu'on n'a pas pris en considération le fait que les valeurs sont influencées par l'appareil utilisé. En conséquence, on suggère que divers composés soient utilisés comme étalons thermiques pour comparer les données de différentes sources. Le mémoire discute également des variables à prendre en considération lorsqu'on tente d'établir de tels étalons et comprend une liste d'étalons thermiques suggérés, couvrant les domaines 100–400° et 1050–1060°.

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APPLICATION OF RADIOISOTOPES IN COLUMN CHROMATOGRAPHY ON SUBSTITUTED CELLULOSES—III

THE SEPARATION OF GOLD FROM SILVER, IRON AND OTHER METALS

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Summary—The chromatographic behaviour of several metals has been studied on columns of natural and substituted celluloses, by using radioisotopes. It has been found that gram and nanogram amounts of gold are not adsorbed on natural cellulose, and consequently gold can be separated from nanogram amounts of silver, iron, zinc, cadmium, chromium, manganese and cobalt. Gold has a limited tendency to form complexes with the functional groups of the celluloses, but the other metals mentioned formed very stable complexes. The results have also been compared with those obtained for mercury.

THE most important studies on the chromatography of traces of metals on cellulose columns deal with the purification of mercury and uranium. Mercury is not adsorbed from ethyl ether onto natural cellulose and is not retained on substituted celluloses: apparently it cannot be adsorbed and cannot form complexing bonds with the amine, phosphate and carboxyl groups.[1] The chromatography of uranyl nitrate in ether on natural cellulose has been studied carefully,[2] and uranium has been found not to be retained on natural cellulose. On the other hand, caesium, strontium, barium, indium and antimony;[2] scandium, yttrium and the lanthanons;[3] chromium, manganese and iron;[2] cobalt;[2,4] copper and silver;[2] zinc;[1,2] and cadmium[1,2,3] are retained more or less strongly. These metals are distributed over all the metal groups of the periodic table, and at present there is no explanation of their retention on cellulose. A comparative study of the other metals might eventually confirm the hypothesis that complexes are formed, and allow the structure and the stability of the complexes of certain metals with the functional groups of the celluloses to be determined. Even before a complete theory of the chromatography of metals on celluloses can be established, however, the results available permit important separations of traces of metals and purification of macro amount of salts to be made.

The separation of gold is important for two purposes: the recovery and concentration of traces of gold from solutions containing traces of other metals, and the purification of macro amounts of gold. These operations can be of importance both in preparative and analytical chemistry. One of the most interesting fields requiring rapid separation of gold, generally on microscopic samples, is archaeology;[5] others include the analysis of cosmic dust,[6] metallurgy of gold,[7] and activation analysis of high purity materials.[8] For preparative purposes, macro amounts of gold may have to be purified before use in electronic instrumentation or after recovery from waste solutions.

Few papers on the ion-exchange chromatography of gold have been published. These include articles on ion-exchange papers in mixed solvents,[9] ion-exchange resins,[10] and papers pretreated with organic complexing agents.[11]

A booklet on the radiochemistry of gold[12] and a recent review on ion-exchange celluloses[13] contain further references: among these is the only article dealing with a kind of chromatography of gold on columns of natural cellulose.[14] Gold was adsorbed on 2 g of natural cellulose containing hydrochloric or nitric acid and this was then packed at the top of a column of cellulose, and the gold eluted with ethyl acetate. The amount of gold used was 0·0050–0·1857 g; the amounts of other metals were not indicated, their movement into the column was not specified, and no method for their recovery was given. Although the authors stated that preliminary separations of gold on columns of cellulose were carried out with ethereal solvents, they did not explain why ethyl acetate was finally adopted, and ether no longer used. Indeed, ethyl ether seems to be very useful for eluting gold from cellulose, because many compounds of gold are very soluble in it.

The present study was made in order to apply a unique simple chromatographic procedure to gram and nanogram quantities of gold, and to recover microgram and nanogram quantities of iron, silver and other transition metals, separated from gold. Moreover, the knowledge of the chromatographic behaviour of these metals may contribute to the study of the ion-exchange mechanism on substituted celluloses in ethyl ether solvents, and to the study of the complexing capacity of the different functional groups of these celluloses.

EXPERIMENTAL

Reagents

Reagent-grade chemicals and solvents were used for the preparation of all solutions.
Anhydrous ethyl ether, used as supplied.
Nitric acid (90%) 2% v/v solution ethyl ether.
Ammonium thiocyanate solution, 0·04% w/v in methanol–ethyl ether (1 + 4).
Ammonium thiocyanate solution, 5% w/v in methanol–ethyl ether (1 + 4).
Hydrochloric acid, 3*M*.
Ammonia solution, 3*M*.
Chloroauric acid, $HAuCl_4 \cdot 3H_2O$, crystals.

Cellulose powders

Whatman CF 11 (natural), DE 11 (diethylaminoethyl), AE 11 (aminoethyl), P 11 (phosphate), CM 11 (carboxymethyl), and ET 11 (epichlorohydrin triethanolamine, Ecteola).

Radioisotopes

The gold-198 and silver-110 m were supplied by the Radiochemical Centre, Amersham, England; the others by New England Nuclear Corp., Boston, Mass., U.S.A. The isotopes used are listed in Table I.

The isotope solutions were diluted with 90% nitric acid, and volumes between 10 μl and 250 μl were added to 25 ml of ethyl ether.

Radioactivity measurements

The fractions of eluate and the cellulose powders were collected in plastic bottles of uniform shape and capacity. Their radioactivity was measured by a 128-channel gamma-ray spectrometer ND-110 electronically coupled to an NaI(Tl) crystal, and compared with a standard. The mean dispersion of repeated results was 8%.

Preparation of the columns of celluloses

The columns (10 mm bore; reservoir 200 ml; Teflon stop-cock) were prepared as described earlier.[1,4] The time needed for preparing two columns and running two complete separations is 1 hr.

TABLE I.—RADIOISOTOPES USED IN CHROMATOGRAPHY

	Specific activity at time of use, $Ci.g^{-1}$	Chemical purity, %	Quantity used for each experiment, g
^{198}Au	3	n.s.	$4 \cdot 10^{-8}$
^{110m}Ag	1	n.s.	$1 \cdot 10^{-7}$
^{65}Zn	5·6	99%	$1 \cdot 10^{-8}$
^{109}Cd	carrier-free	99%	$<6 \cdot 10^{-9}$
^{51}Cr	36	99%	$5 \cdot 10^{-8}$
^{54}Mn*			$\sim 10^{-8}$
^{59}Fe	6	99%	$1 \cdot 10^{-7}$
^{60}Co	61	n.s.	$1 \cdot 10^{-8}$

* Produced from the iron solution by $^{54}Fe(n,p)^{54}Mn$.
n.s. = none stated.

Preparation of concentrated solutions of gold

Chloroauric acid crystals were kept in a desiccator and dissolved in ethyl ether just before use. The radioactive gold and the other radioisotopes were added to this solution. No precipitation of silver occurred.

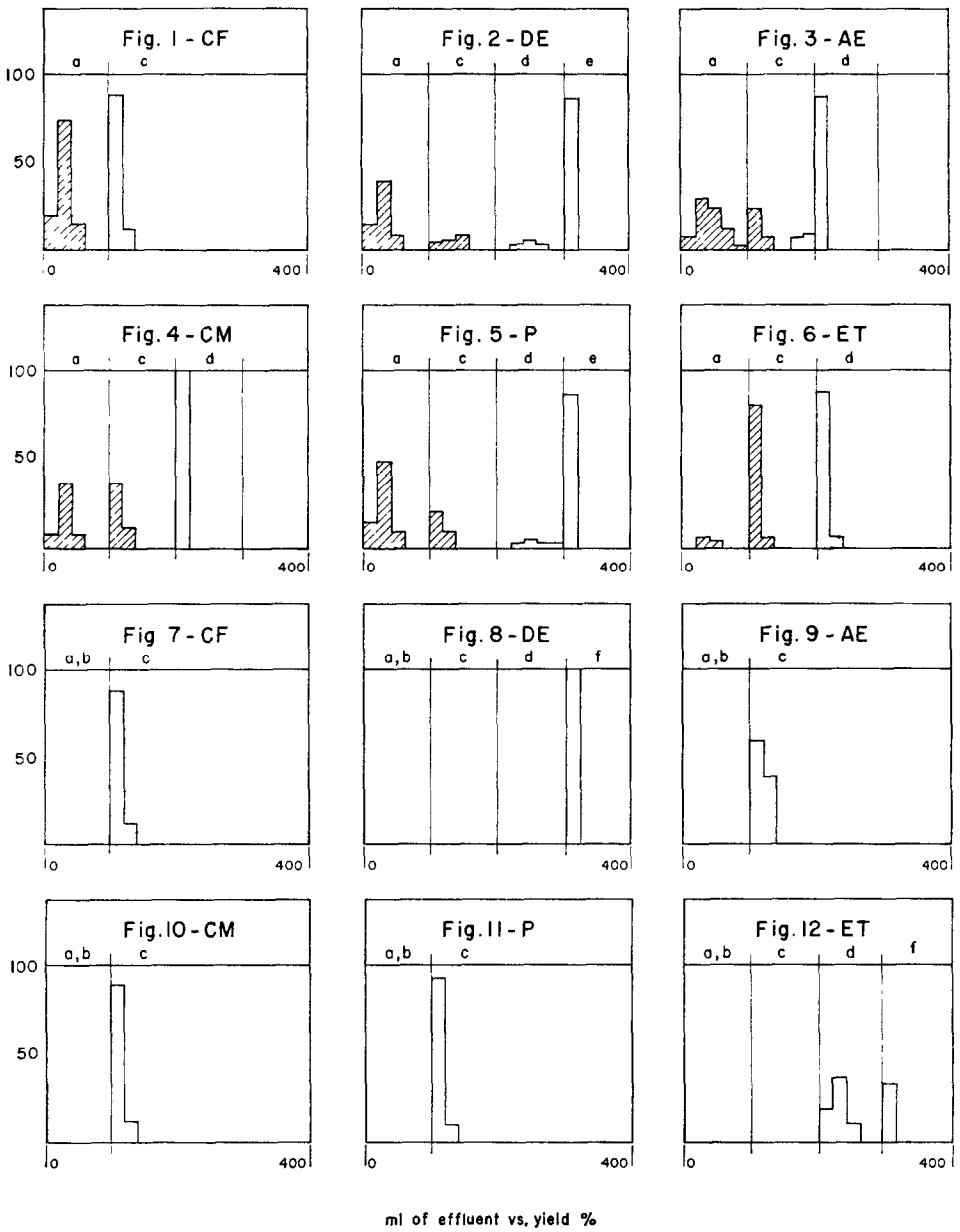
Nitratoauric acid, $H\,Au(NO_3)_4$ was prepared by making auric oxide[15,16] and dissolving it in hot 90% nitric acid. One ml of this solution was added to 50 ml of ethyl ether, already containing the radioisotopes, just before the chromatography. Traces of peroxides formed by the action of nitric acid on ethyl ether, can reduce gold(III) to the metal in a short time. The solution was passed through the column at very high speed, by using compressed air, in order to avoid prolonged contact of cellulose with the nitratoauric acid. The flow-rate of 50 ml/min did not affect the retention of traces of metals.

RESULTS AND DISCUSSION

Gram or nanogram amounts of gold (as chloroauric acid) are not adsorbed on natural cellulose and pass quantitatively through the column (Fig. 1). On the other hand, substituted celluloses partially retain gold (Figs. 2–6). Ecteola cellulose (Fig. 6) gives the highest retention, though even this is incomplete. In any case gold can be quantitatively eluted by 0·04% ammonium thiocyanate solution.

Nanogram quantities of chromium, manganese and iron are completely retained on all celluloses and separated from gold. Their retention has been studied in the standard conditions chosen for cobalt,[4] and the results for iron are shown in Figs. 1 to 6. Chromium and manganese behave practically the same as cobalt.[4] The retention of nanogram amounts of iron was affected by the presence of gram amounts of chloroauric acid: iron was carried by the gold and passed through the column. This interference was overcome by using nitratoauric acid on a longer column (25 × 1 cm) instead of chloroauric acid: in these conditions the separation of gold from iron was quantitative, and the elution curves of iron were closer to those of iron when alone. Occasionally during separation of gram amounts of nitratoauric acid from iron, reduction of gold occurred at a certain extent (5–10%) on the column, and some purple of Cassius was visible. In this case it was possible to continue the regular procedure, elute the other metals, and recover the pure precipitated gold by ashing the cellulose.

Zinc and cadmium were perfectly separated from gold on the natural, phosphate, and aminoethyl celluloses, giving the elution curves already reported,[1] and their chromatography was not appreciably affected by the presence of large quantities of chloroauric or nitratoauric acids. It was also possible to separate zinc and cadmium from silver on aminoethyl and phosphate celluloses. Corresponding figures in this



FIGS. 1–6.–The chromatographic behaviour of gold (shaded area) and iron on columns of celluloses.

Solvents: (a) anhydrous ethyl ether, (b) nitric acid (90%) 2% v/v solution in ethyl ether, (c) ammonium thiocyanate, 0·04% w/v solution in methanol–ethyl ether (1 + 4), (d) ammonium thiocyanate, 5% w/v solution in methanol–ethyl ether (1 + 4), (e) 3*M* hydrochloric acid, (f) 3*M* ammonia.

Whatman celluloses: CF—natural, DE—diethylaminoethyl, AE—aminoethyl, P—phosphate, CM—carboxymethyl, ET—Ecteola.

FIGS. 7–12.–The chromatographic behaviour of silver on columns of cellulose. For legend see Figs. 1–6.

paper and the earlier two of this series,[1,4] can be superimposed to study the possibility of separations of nanogram amounts of the metals.

Silver was retained by all celluloses. The elution curves from the natural, carboxymethyl and phosphate celluloses, (Figs. 7, 10 and 11), have the same shape and this should mean that carboxymethyl groups and phosphate groups are not responsible for retention of silver: on these three celluloses, silver is simply adsorbed. On the contrary, celluloses containing amino groups, namely diethylaminoethyl (Fig. 8), aminoethyl (Fig. 9), and epichlorohydrin-triethanolamine (Fig. 12), retain silver much more strongly because they evidently form amino complexes, the highest strength being for diethylaminoethyl complexes, as expected. A 5% solution of ammonium thiocyanate did not elute silver, although thiocyanate is a good complexing agent for silver and has been often used to elute silver from ion-exchange resins. In fact, aqueous ammonia was needed to elute silver from diethylaminoethyl cellulose. These results again emphasise the peculiarity of the behaviour of mercury under these chromatographic conditions: mercury should form amino complexes and therefore should be retained at least by diethylaminoethyl cellulose; on the contrary it does not, so mercury can be separated from silver on all celluloses. Mercury cannot be separated quantitatively from gold, but on Ecteola cellulose about 30% of the gold passed through with the mercury, and 70% of the gold was retained (Fig. 6) free from mercury.

Antimony and copper could also be separated from gold and their behaviour will be illustrated in the next articles of this series.

Gold was obtained in ethyl ether solution after passage through cellulose columns: it was generally easy to reduce the gold to metal by exposing the nitratoauric acid to sunlight or by adding some nitric acid to the solution of chloroauric acid in ether.

CONCLUSIONS

Traces of gold can be separated from many elements by chromatography on a natural cellulose column. Gram amounts of gold can be freed from traces of metals by a simple and rapid procedure. It is interesting to note that gold behaves like mercury and uranium on natural cellulose and its chromatography is not affected by the anions present. The traces of metals collected on the cellulose column can be eluted, sometimes selectively, and subsequently analysed by neutron-activation or other physico-chemical methods. In special cases substituted celluloses can be used for particular separations. Gold tends to be retained on substituted celluloses, but at present no explanation can be given of this retention.

It is very important to note that silver forms very strong bonds with the amino groups of the substituted celluloses and the chromatographic behaviour of silver is markedly different from that of mercury, which is not retained on substituted celluloses although mercury generally forms stable amino complexes. Other transition metals such as chromium, manganese, iron and cobalt form amino complexes, and they are more or less strongly retained on substituted celluloses, but as it is known that the complexes of silver are quite different from those of cobalt, it should be interesting to elucidate the nature of the complexes of these metals with the aminoethyl, diethylaminoethyl, and triethanolamine groups of the substituted celluloses.

The study of the structures, stability constants and other parameters of these complexes seems of interest. Even though the distribution of the functional groups

on these celluloses is not thoroughly known, these modified polymers are derived from relatively simple natural polymers and have points of similarity to both sugars and proteins. The study of the selective retention of traces of metals could be of interest not only to analytical chemists but also to biochemists.

Finally, the particular ability of each type of cellulose to retain the metals shows that in common with most separations on cellulose, simple partition chromatography is not the sole mode of separation, but that strong adsorption phenomena, together with complex-formation, depending on the type of cellulose, may also be important factors.

Acknowledgement—The author expresses his appreciation to the National Research Council of Canada for financial support of this research (Grant No. 734, 1965).

Zusammenfassung—Chromatographischen Verhalten von manchen Metallen an der Cellulosesäule und modifizierten Cellulosesäulen wurde mit Radioisotoptechnik untersucht. Diese Untersuchung zeigte das der Gold im Menge von Gramm bis vierzig Nanogramme wird an der Cellulose nicht absorbiert und folglich kann doch von Silber, Eisen, Zink, Kadmium, Chrom, Mangan und Kobald abgetrent werden. Der Gold zeigt eine sehr beschränkte Tendenz zur Komplexbildung mit der Cellulose, während der andere obengenante Metalle bilden sehr stabile Komplexverbindungen. Die erlangten Resultate wurde auch auf das Quecksilber betreffenden Resultate bezichen.

Résumé—Les radioisotopes ont été appliqués à l'étude du comportement chromatographique de plusieurs métaux sur colonnes de cellulose naturelle et de celluloses substituées. On a constaté que l'or en quantités variables entre un gramme et quelques nanogrammes n'est pas adsorbé sur cellulose naturelle, et qu'il est par conséquent séparé d'avec nanogrammes d'argent, fer, zinc, cadmium, chrome, manganèse et cobalt. La tendance à former des complexes avec les groupes fonctionnels des celluloses substituées est très limitée dans le cas de l'or, tandis que les autres métaux cités forment des complexes très stables. Les résultats obtenus ont été aussi referés aux résultats concernant le mercure.

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HYDROLYSIS STUDY OF ORGANIC ACID ANHYDRIDES BY DIFFERENTIAL THERMAL ANALYSIS—II

MALEIC ANHYDRIDE AND TRIMELLITIC ANHYDRIDE

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Summary—Differential thermal analysis has been used to follow the hydrolysis of maleic anhydride (MA) and trimellitic anhydride (TMA). On exposure of MA to an atmosphere of 96% relative humidity, maleic acid is produced, hydrolysis being complete in 21 hr at 22°, but no hydrolysis occurs at a relative humidity of 50%. When exposed to an atmosphere of 96% relative humidity, TMA is quite stable for short periods, but hydrolyses slowly, the production of trimellitic acid being complete in 113 hr at 22°.

IN a previous paper in this series,[1] differential thermal analysis (DTA) was applied to the study of the hydrolysis of pyromellitic dianhydride. The present paper is a continuation of this work, DTA being applied to a study of the hydrolysis of two additional commercially-important anhydrides, maleic and trimellitic anhydrides.

EXPERIMENTAL

Apparatus and reagents

The apparatus employed was identical to that previously reported.[1] The maleic anhydride, a commercial product obtained from the Monsanto Chemical Company, was specified as briquettes melting at 57–60°. Maleic acid was obtained from Matheson, Coleman and Bell, and it had a melting point of 135–6°. The trimellitic anhydride, also a commercial product, was obtained from Amoco Chemicals Corp. in the form of flakes melting at 161–163·5°. Trimellitic acid, a product of the K & K Laboratories, Inc., melted over the range 218–220°. All materials were ground in an atmosphere of dry nitrogen to 10 μ average particle size.

Procedure

DTA curves were obtained from 2-mg samples of each anhydride, both as received, and after exposure to relative humidities of 96 and 50% at 22·34–23·22°. The reference material was calcined alumina. Samples were heated at 10°/min while a stream of nitrogen passed through the bedded powder sample. All DTA curves were prepared at a sensitivity of 300 μV/(6°).

RESULTS AND DISCUSSION

Figure 1 is a reproduction of the DTA curve obtained from maleic anhydride and shows two endothermic peaks. The first of these, with a maximum at *ca.* 60°, is in excellent agreement with that reported by Sandermann *et al.*[2] and with the reported melting point for the compound.[3] The second peak marks the volatilization of the anhydride, as confirmed by the observation that the sample holder was empty when the curve returned to its base line.

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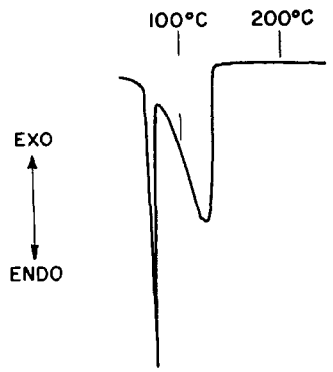


FIG. 1.—DTA curve for maleic anhydride.

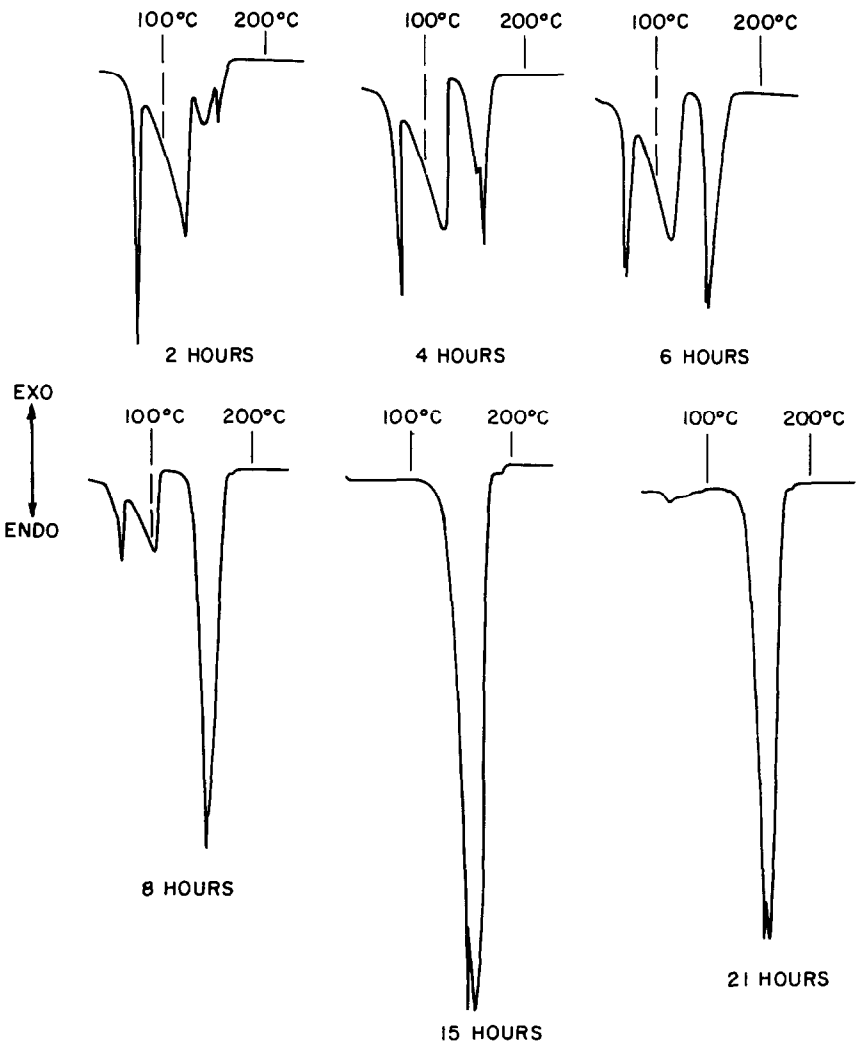


FIG. 2.—DTA curves for maleic anhydride after exposure to 96% relative humidity for various times.

DTA curves for samples of maleic anhydride exposed to 96% relative humidity for various periods of time are reproduced in Fig. 2. It is evident from these curves that the maleic anhydride peaks diminish in intensity with the length of exposure, and become virtually non-existent after 21 hr. The exposure to this atmosphere also induces two peaks at higher temperatures, which are well resolved at the short exposure times but tend to fuse into a single peak as the exposure time is extended. This sharp single endotherm corresponds well with the endotherm for maleic acid which is shown in Fig. 3. The first of the higher-temperature peaks is associated with the melting of the maleic acid, reported to be 130–131°,[3] while the second is associated with decomposition of this compound, which is reported to occur at 135°.

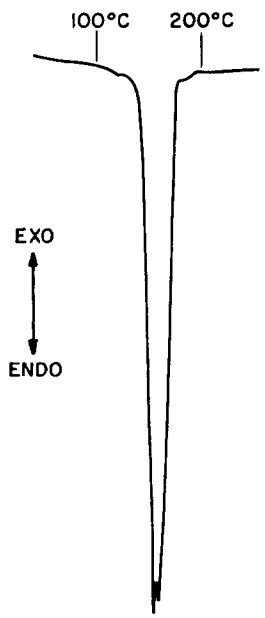
In contrast to the results obtained at 96% relative humidity, exposure of maleic anhydride to 50% relative humidity for 46 hr produced no variations from the curve for maleic anhydride.

While these results indicate that maleic anhydride can undergo hydrolysis, they also show that the material can be stored safely at 50% relative humidity at temperatures up to 22°.

Figure 4 depicts the DTA curve obtained from trimellitic anhydride, which is characterized by two endothermic peaks. The first of these, occurring at *ca.* 165°, is in good agreement with the reported melting point for this compound, 165–7°.[4] The second endotherm will be discussed subsequently.

DTA curves for 2-mg samples of trimellitic anhydride exposed to 96% relative humidity for various periods are reproduced in Fig. 5. These results are to be compared with the curve for trimellitic acid which is reproduced in Fig. 6.

It is evident from the curves that short periods of exposure to 96% relative humidity have little effect, the curve (Fig. 5*a*) being identical with that of the anhydride.



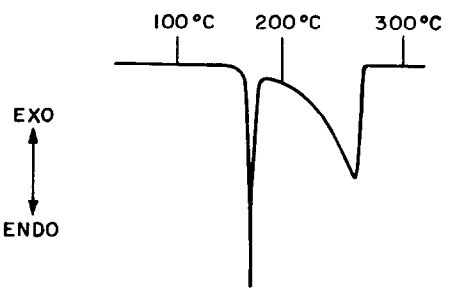


FIG. 4.—DTA curve for trimellitic anhydride.

FIG. 3.—DTA curve for maleic acid.

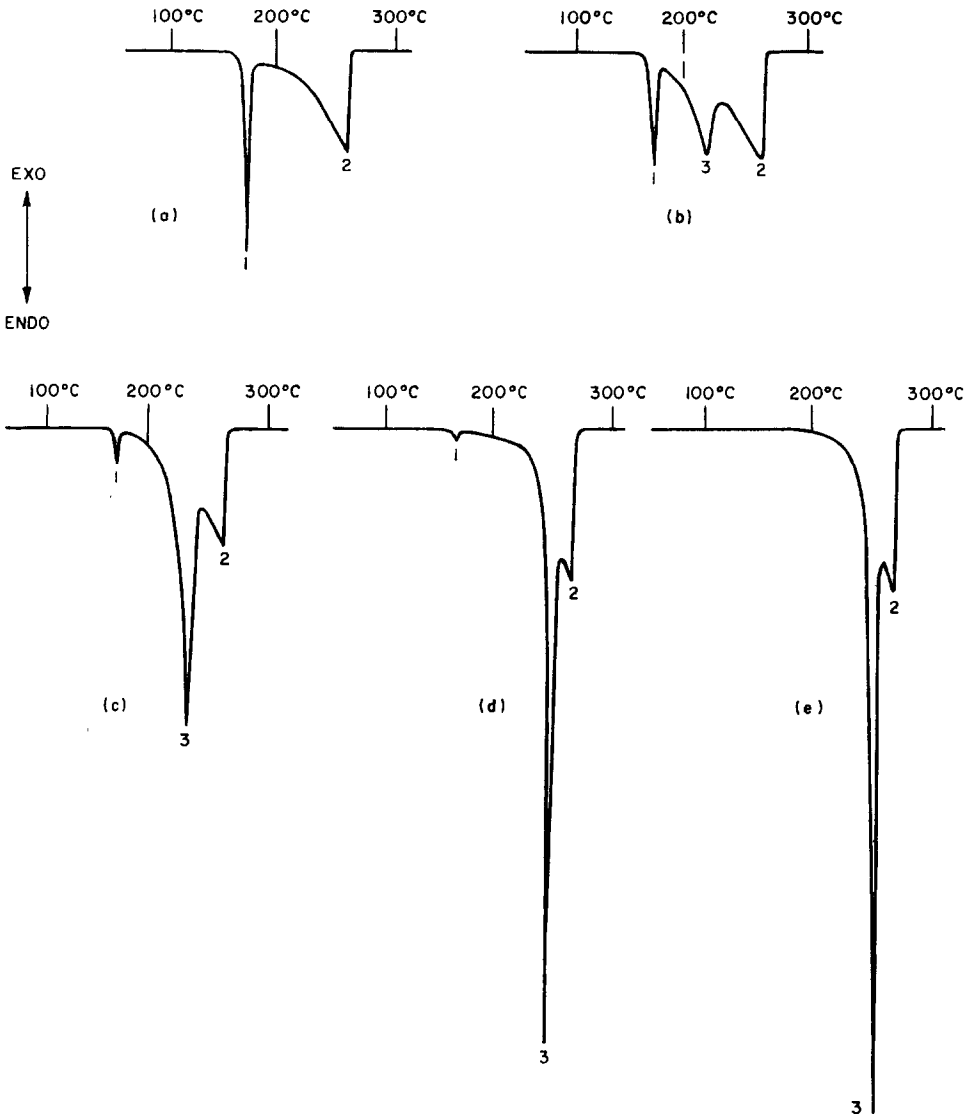


FIG. 5.—DTA curves for trimellitic anhydride after exposure to 96% relative humidity for various times.
(*a*) 7 hr; (*b*) 16 hr; (*c*) 48 hr; (*d*) 72 hr; (*e*) 113 hr.
1—Trimellitic anhydride m.p., 161°C
2—Trimellitic anhydride b.p., 240°C
3—Trimellitic acid m.p., 216°C.

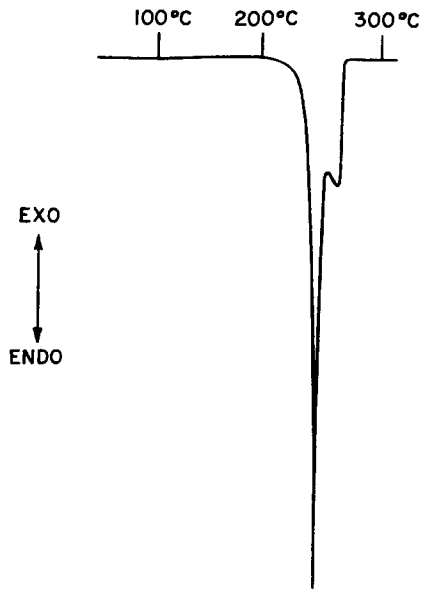


FIG. 6.—DTA curve of trimellitic acid.

However, as the exposure period increases, several changes in the curves are observed. The first of these is the decrease in intensity of the melting endotherm for trimellitic anhydride, indicating hydrolysis of the anhydride ring. This peak disappears completely after 113 hr of exposure. A third endotherm appears after 16 hr of exposure to 96% relative humidity, and becomes more intense with the extent of exposure. This endotherm occurs at the melting point of trimellitic acid, 215–217°,[5] as shown by the excellent correspondence of Figs. 5*e* and 6. The lack of better temperature correspondence in materials subjected to shorter exposure periods is assumed to be a result of melting point lowering induced by the anhydride.

The third endotherm, with a peak at 260°, appears in DTA curves for both the hydrolysed and unhydrolysed material without any significant variation. The breadth of this peak (Fig. 4), which is subdued by competitive endothermic reactions in the hydrolysed material (Figs. 5*e* and 6), would indicate volatilization similar to that experienced with maleic anhydride. As trimellitic acid is reported to decompose at its melting point,[5] this peak is assumed to result from an impurity. The significance of this peak was not investigated.

As previously indicated,[1] differential thermal analysis can be applied successfully to the determination of safe storage conditions of moisture sensitive materials. Further, the sensitivity, quantities of materials employed, and the speed of the technique would appear to offer advantages not available in other methods now employed for this purpose.

Acknowledgement—The authors are indebted to Mrs. M. B. Warner for her assistance in the preparation of the DTA curves and to Dr. E. L. Simons for his helpful discussions of this work.

Résumé—On a utilisè l'analyse thermique différentielle pour suivre l'hydrolyse de l'anhydride maléique (MA) et de l'anhydride trimellitique (TA). Lorsqu'on expose MA à une atmosphère à 96% d'humidité relative, il se forme de l'acide maléique, l'hydrolyse ètant complète en 21 h à 22°, mais il n'y a pas d'hydrolyse avec une humidité relative de 50%. Par exposition à une atmosphère à 96% d'humidité relative, TA est totalement stable pendant de courtes périodes, mais s'hydrolyse lentement, la production d'acide trimellitique étant complète en 113 h.

Zusammenfassung—Die Hydrolyse von Maleinsäureanhydrid (MA) und Trimellitsäureanhydrid (TA) wurde mittels Differential thermoanalyse verfolgt. Setzt man MA einer Atmosphäre von 96% relativer Feuchtigkeit aus, so bildet sich Maleinsäure, wobei die Hydrolyse bei 22° in 21 Stunden beendet ist; bei einer relativen Feuchtigkeit von 50% hingegen tritt keine Hydrolyse ein. In einer Atmosphäre von 96% relativer Feuchtigkeit ist TA für kurze Zeiten recht stabil, hydrolysiert aber langsam; die Bildung von Trimellitsäure ist nach 113 Stunden vollständig.

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COMPLEXOMETRIC DETERMINATION OF GALLIUM WITH CALCEIN BLUE AS INDICATOR

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Summary—A metalfluorechromic indicator, Calcein Blue, has been used for the back-titration of milligram amounts of EDTA in presence of gallium complexes. The indicator was used in conjunction with an ultraviolet titration assembly equipped with a cadmium sulphide detector cell and a microammeter for enhanced end-point detection. The result is a convenient and rapid method with an accuracy approaching 0·1% and a relative standard deviation of about 0·4% for 10 mg of gallium.

VARIOUS indicator and titrant systems have been used for the complexometric determination of milligram amounts of gallium with EDTA. For the direct titration of gallium with EDTA, indicators such as Gallocyanine,[1] PAN,[2,3] PAR,[2] copper-PAN,[4,5] SNAZOXS,[6] 7-(1-naphthylazo)-8-hydroxyquinoline-5-sulphonic acid,[7] Pyrocatechol Violet[8] and Morin[8,9] have been used. These titrations were carried out in the pH range 1–5, and most involved heated titrand solutions.

Indirect complexometric determinations of gallium with EDTA have involved indicators such as Pyrocatechol Violet with bismuth nitrate as the titrant,[10,11] Xylenol Orange with various titrants,[12] Xylenol Orange plus Poirrier's Blue with thorium nitrate as the titrant,[13] Pyrogallol Red and Bromopyrogallol Red as indicators with bismuth nitrate as the titrant,[14] Erio Black T as indicator with zinc as the titrant,[15] SNAZOXS as indicator with copper as the titrant,[16] and diphenylcarbazone plus Methylene Blue as indicator in the presence of the vanadium-EDTA complex with zinc acetate as the titrant.[17]

There are two disadvantages of visual EDTA titrations: many EDTA complexes are coloured, making the end-point hard to observe, and often the indicator change at the end-point is not sharply defined. Use of a fluorescent indicator would eliminate at least the first of these difficulties. Of the indicators cited above, only Morin was used as a fluorescent indicator.[8] Gallium-EDTA complexes are only slightly coloured, but dissatisfaction with the highly coloured indicator used by Miner and DeGrazio[13] led to exploration of the use of fluorescent indicators, in particular, metalfluorechromic indicators. These indicators function in highly coloured solutions by forming a metal complex and at the same time undergoing a change in the intensity and sometimes the colour of fluorescence.[18] Their extreme sensitivity allows the determination of small concentrations of many metals, often without preliminary separations, and macro samples may be conveniently titrated.

The first use of a metalfluorechromic indicator, as such, was by Wilkins[18] for the indirect chelometric determination of cobalt and iron. He complexed the metals with an excess of EDTA at pH 4·0 and back-titrated with standard copper solution under ultraviolet light, using an indicator known as Calcein. The second known use

of Calcein as a metalfluorechromic indicator was also by Wilkins[19] for the back-titration of EDTA in the presence of the highly-coloured EDTA complexes of cobalt, chromium and copper. Calcein, which is a condensation product of fluorescein, iminodiacetic acid, and formaldehyde, was first used as an indicator by Diehl and Ellingboe,[20] and Tucker.[21] They used it as a visual indicator in a direct complexometric titration, and not as a metalfluorechromic indicator.

The second useful metalfluorechromic indicator was then known as Calcein W, a purified form of Calcein containing no free fluorescein to cause residual fluorescence and fuzzy end-points.[22] It was first used by Hibbs and Wilkins[23] for the indirect determination of aluminium, titanium, nickel and other constituents of their alloys and by Wilkins and Hibbs[24] for the direct determination of copper with triethylenetetramine without prior separations or the use of masking agents.

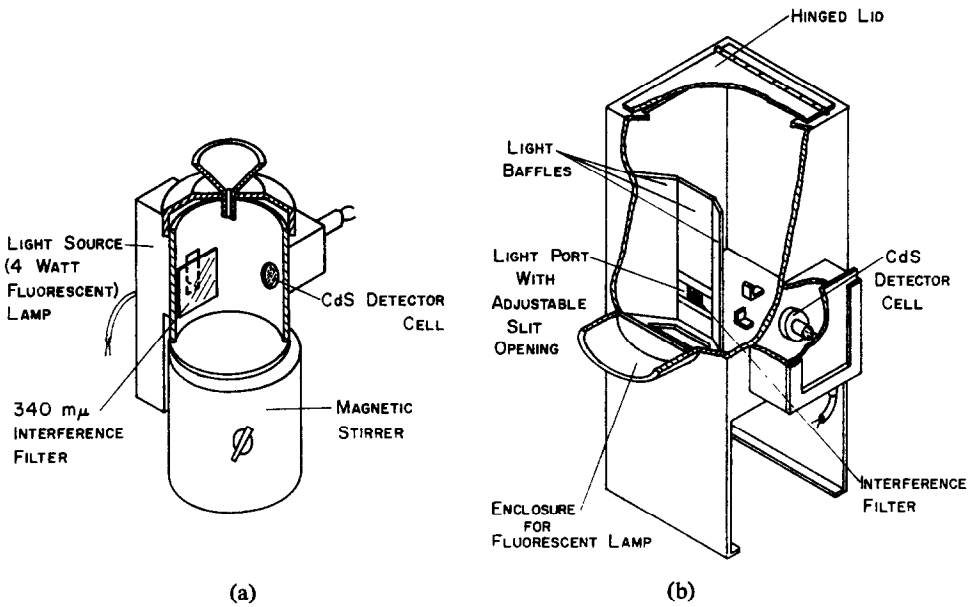

FIG. 1.—Ultraviolet titration assembly for the determination of gallium using a metalfluorechromic indicator.
(a) Original design. (b) Modified design.

A metalfluorechromic indicator somewhat different in structure, but similar in properties to Calcein W, is Calcein Blue. It is a condensation product of methyl-umbelliforone, formaldehyde and iminodiacetic acid. Calcein Blue is reported by Wilkins[25] to be superior to Calcein W for chelatometric titrations. This is because the wavelengths at which Calcein Blue is activated in acidic or basic solution are a much closer match to the wavelength of maximum output of most ultraviolet sources than are the excitation wavelengths of Calcein W. Calcein Blue was first used by Wilkins[25] for the direct determination of calcium, strontium and barium and the indirect determination of nickel and chromium mixtures without prior separations.

Because of the superiority of Calcein Blue used indirectly, it was chosen by us as an indicator for the investigation of the indirect complexometric determination of gallium. Standard copper solution was used as the titrant for the excess of EDTA.

Wilkins[26] used a titration housing of rather simple design to permit the visual detection of the fluorescent end-point. A commercial version of the equipment is available.[27] In our laboratory a titration housing was used which monitored the course of the titration by means of a microammeter connected in series with a cadmium sulphide detector cell located at right angles to the incident ultraviolet radiation. Calcein Blue fluoresces at 445 mμ, which is close to the wavelength of maximum response for cadmium sulphide detector cells. This equipment gave better end-point detection than could be obtained visually. The apparatus is shown in Fig. 1*a*, and a later modification with a more powerful ultraviolet source and better access to the titration cell and the detector cell is shown in Fig. 1*b*.

EXPERIMENTAL

Reagents

Standard 0·1M *EDTA*, prepared from disodium ethylenediaminetetra-acetate dihydrate dried according to the method of Schwarzenbach.[28]

Standard 0·025M *copper*(II), prepared from pure copper dissolved in concentrated nitric or sulphuric acid and standardized against the standard EDTA solution.

Indicators. Calcein Blue, 0·1% aqueous solution; Bromphenol Blue, 0·1% aqueous solution.

Buffer. Sodium acetate-acetic acid buffer solution, pH 4·8.

Sodium hydroxide, 6M

Hydrochloric acid, 0·5M

All chemicals were of reagent grade purity.

Apparatus

The titration assembly and its circuitry are shown in Figs. 1 and 2 respectively.

A Koch microburette, graduated in 0·01 ml divisions, and readable to 0·005 ml, was used for the titrations.

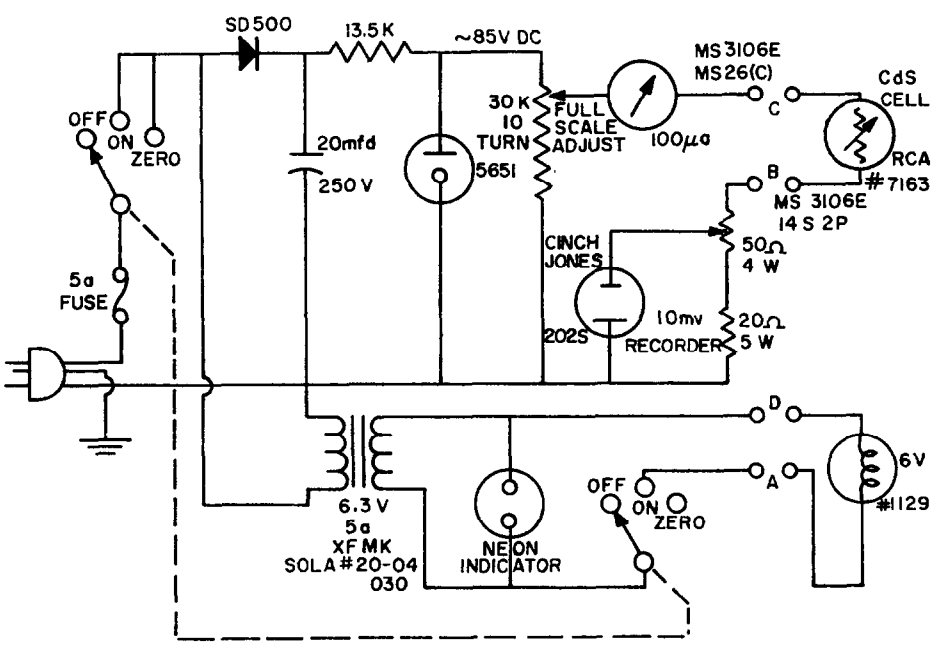

FIG. 2.—A schematic diagram of the electrical circuitry for the ultraviolet titration assembly.

Procedure

The following procedure is recommended for solutions free from interfering ions or for solutions in which the interfering ions have been suitably masked. Transfer an aliquot containing 1–20 mg of gallium into a Berzelius beaker containing 50 ml of 0·5*M* hydrochloric acid. Aliquots of 1 ml or less are desirable in order to minimize the amount of base added later. Dilute the solution to 95 ml with distilled water. If a pH meter is used, add 6*N* sodium hydroxide until the meter indicates a pH of 3·5. Otherwise, add 2 drops of Bromphenol Blue and add base until the colour of the solution just begins to change. Add 15 ml of buffer solution to bring the pH of the solution to about 4·8, then add 5 ml of 0·1*M* EDTA from an automatic-delivery pipette. Add 7 drops of Calcein Blue indicator solution and boil for 2 min. Cool to near room temperature and titrate with the 0·025*M* copper solution. Follow the course of the titration with the microammeter of the titration assembly, the microammeter being adjusted to read 100% fluorescence initially. The fluorescence initially decreases rapidly, then more slowly until the end-point is reached, when a sharp drop in fluorescence occurs.

Determine the end-point either graphically or by direct observation of the meter. A typical titration curve is shown in Fig. 3.

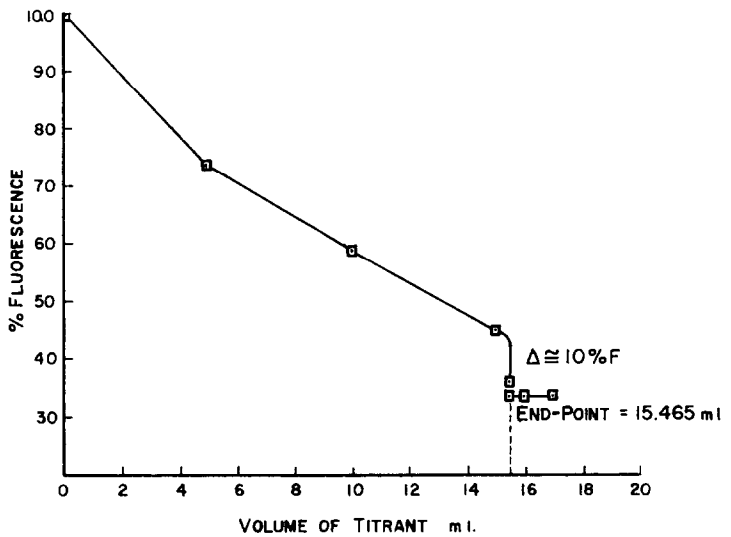

FIG. 3.—A typical titration curve for the back-titration of gallium, with Calcein Blue as indicator.

The characteristic meter response can be determined from the standardization titrations and then the end-point can be anticipated for titrations of unknown solutions. It is possible to titrate rapidly to a meter reading approximately 10–15 units greater than that at the end-point, and then titrate drop by drop until an abrupt needle deflection of 5–10 units occurs. If no significant deflection occurs with the addition of further titrant, the end-point has been reached. Normally the fluorescence will remain constant for excesses of titrant up to 1 or 2 ml.

If aliquots containing 20–100 mg of gallium are to be titrated, more 0·1*M* EDTA solution must be added and 0·05*M* copper solution should be used for the back-titration.

RESULTS AND DISCUSSION

Three series of determinations were made in order to measure the precision of the method. In Series C the accuracy was also measured. The end-points in Series A were obtained graphically and those in Series B and C were obtained visually from the behaviour of the microammeter. A summary of the results is shown in Table I.

The relative standard deviations of Series A, B and C, based on the measurement of the volume of titrant added, were 0·11%, 0·14% and 0·19% respectively. The results from Series A demonstrate the slightly greater precision obtainable from

TABLE I.—PRECISION STUDIES ON THE CALCEIN BLUE INDICATOR METHOD FOR THE COMPLEXOMETRIC DETERMINATION OF GALLIUM

Series	n	Gallium found, *mg*	Standard deviation, *mg*	Relative standard deviation, %
A	22	9·320	$0·026_8$	0·29
B	16	9·334	$0·034_8$	0·37
C	10	9·977	$0·047_1$	0·47

graphical end points. Application of the *F*-test to the data of Series A and B led to the conclusion that at the 95% confidence level there is no statistically significant difference in the precision between the two sets of data. A *t*-test showed that the difference between the mean amount of gallium in Series A and B was not significant.

The accuracy of the procedure was checked by using calibrated pipettes and carefully standardized solutions. From the mean value of standard copper solution used in Series C, the amount of gallium found experimentally was 9·98 mg. The theoretical amount of gallium present was 9·99 mg. Thus the deviation from the theoretical in this series was only 0·1%.

A convenient, rapid, precise and accurate method for the titration of gallium has been developed. The use of Calcein Blue affords a titration with a sharp end-point in contrast to some of the previous methods. The use of the apparatus described could be conveniently applied to other fluorescent titrations in lieu of direct visual observation of the end point.

The work reported was performed under U.S. Atomic Energy Commission Contract AT(29-1)-1106.

Zusammenfassung—Ein fluoreszierender Metallindikator, Calceinblau, wurde zur Rücktitration von Milligrammengen komplex an EDTA gebundenen Galliums verwendet. Der Indikator wurde in Verbindung mit einem Ultraviolett-Titrationsgerät verwendet, das mit einem Cadmiumsulfiddetektor und einem Mikroamperemeter zur verbeserten Endpunktsbestimmung ausgerüstet ist. Es resultiert ein bequemes und schnelles Verfahren mit einer Genauigkeit von fast 0,1% und einer relativen Standardabweichung von etwa 0,4% für 10 mg Gallium.

Résumé—On a utilisé un indicateur métallofluorochrome, le Bleu de Calcéine, pour le dosage en retour de EDTA en présence de sa gallium-complex en quantités de l'ordre du milligramme. On a utilisé l'indicateur en liaison avec un montage de titrage en ultra-violet équipé d'une cellule de détection au sulfure de cadmium et d'un microampéremètre pour une détection plus sensible du point de fin de dosage. Le résultat en est une méthode commode et rapide avec une précision approchant 0,1% et un écart type relatif d'environ 0,4% pour 10 mg de gallium.

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FLUORESCENCE AND PHOSPHORESCENCE CHARACTERISTICS OF ANTICOAGULANTS

A NEW APPROACH TO DIRECT MEASUREMENT OF DRUGS IN WHOLE BLOOD

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Summary—Fluorimetric and phosphorimetric excitation and emission peaks and limiting detectable concentrations and phosphorimetric decay times are given for warfarin, dicumarol, diphenandione, phenindione and tromexan. Known concentrations of warfarin, a highly fluorescent compound, and dicumarol, a highly phosphorescent compound, are directly measured in the complex biochemical system of whole blood. Excellent recoveries of warfarin and dicumarol in the concentration range of 0·1 to 10 mg% in whole blood were achieved.

FLUORIMETRY and phosphorimetry have been used previously in the analysis of drugs in biological fluids.[1–7] Both techniques require fewer sampling steps and chemical reagents for analysis than most other instrumental methods. Fluorimetry is a simpler method, is of lower cost, uses simpler instrumentation, and uses a much wider range of solvents than phosphorimetry, whereas phosphorimetry is generally more selective and sensitive than fluorimetry. The disadvantages of phosphorimetry become less important in areas where fluorimetry is not applicable. To illustrate their complementary nature, fluorimetry and phosphorimetry are used here with excellent results for the direct measurement of anticoagulants separated from whole blood. This is not to be interpreted as a proposed clinical procedure; whole blood is used here because it provides an interesting and complex biochemical medium. Warfarin, an intensely fluorescing compound when excited by a xenon source, is measured by fluorimetry. Dicumarol, although it fluoresces, exhibits stronger phosphorescence and so is measured by phosphorimetry.

The analysis of both compounds is made simpler and more accurate by the use of protein-free ethanolic filtrates of whole blood samples. Protein-free ethanolic filtrates were previously[2] used for the phosphorimetric determination of a number of sulpha drugs in serum. The ethanolic filtrate is shown here to work equally well for the phosphorimetric measurement of non-protein-bound anticoagulants in whole blood.

EXPERIMENTAL

Apparatus

Fluorescence measurements were taken with a spectrophotofluorimeter (Aminco-Bowman No. 4-8202) with a potted RCA IP28 photomultiplier tube, a 150-W xenon arc lamp and an X-Y recorder (No. 1620-814, American Instrument Co. Inc.). The same instrumentation modified with a phosphoroscope attachment (Aminco-Keirs No. C27-62140) was employed for all phosphorimetric measurements. All studies were performed at constant slit width, with the slit arrangement 4, 3, 3, 4, 3. A volumetric "repipet" apparatus was used in the preparation of all experimental samples.

Reagents

Ethanol was used as the solvent for all studies. Absolute ethanol was distilled through a 6-ft vacuum-jacketed and silvered column with a reflux ratio of 15:1. The column was packed with 3/8 in.

coil helices. Only the centre fraction of the distillate was saved, and this was checked for acceptable fluorimetric and phosphorimetric backgrounds.

Standard stock solutions of the anticoagulants were prepared by adding 50 ml of absolute ethanol to 50 mg of each of dicumarol, diphenadione, phenindione, tromexan and warfarin. Five drops of di-n-butylamine were added to each stock solution (except phenindione) to aid in the dissolution of the drugs. The di-n-butylamine did not increase the fluorescence or phosphorescence backgrounds when mixed in the same proportions with pure ethanol. Solutions used for the measurement of spectra and for analyses were prepared by dilution of the stock solutions to give the desired concentrations.

Procedure

Excitation and emission spectra were obtained for each compound (except diphenadione and phenindione, which did not fluoresce at a concentration of 1 mg/ml of ethanol) by both fluorimetry and phosphorimetry. The limiting detectable concentrations were determined by fluorimetry and by phosphorimetry, and were taken as that drug concentration which resulted in a signal twice the standard deviation of the background (blank ethanolic solution with no drugs) readings. The fluctuations were due partially to noise but mainly to variability in the source intensity signal during a series of measurements.

"Unknown"drug samples in citrated blood were prepared by mixing 8 ml of absolute ethanol, 1 ml of ethanolic solution of the specified drug (of known concentration), and 1 ml of citrated blood. A blank was prepared by adding 1 ml of citrated blood (containing no drugs) to 9 ml of absolute ethanol. If a volumetric "repipet" is used in the preparation of these 10-ml samples, the order of addition of the blood and the diluent becomes arbitrary and has no bearing on the ease or accuracy of the dilution. The mixtures were shaken for 3–5 min and then centrifuged for 5 min to separate the precipitated protein. Then 1 ml of supernatant liquid was added to 9 ml of absolute ethanol and mixed, and the relative intensity signal of fluorescence or phosphorescence was measured. The relative intensity signals of the "unknowns" were corrected by subtracting the intensity signal due to the blood (the difference between the ethanol background relative intensity signal and the intensity signal of the blood-ethanol blank) from the relative intensity signals of the "unknowns". The concentration of the "unknown" sample was determined by comparing the corrected intensity signal of the "unknown" with that of a standard solution in the same concentration range as that of the "unknown". Fluorimetry was used as the method of choice for the analysis of warfarin in whole blood at concentrations of 0·1 mg/100 ml of blood, 1·0 mg/100 ml of blood and 10 mg/100 ml of blood. Phosphorimetry was the method of choice for dicumarol when analysed by this procedure at the same concentrations as the warfarin.

A number of protein-free filtrate blanks were prepared from whole blood, and their fluorescence and phosphorescence backgrounds were measured.

RESULTS AND DISCUSSION

The primary purpose of this study is to demonstrate that fluorimetry and phosphorimetry can be used to make direct, accurate and rapid measurements of non-protein-bound drug concentrations in the complex biochemical environment of diluted whole blood. Out-dated blood-bank citrated blood was used for the preparation of all blood samples. The ethanolic protein-free filtrates prepared in the course of the analyses are in effect dilutions of the whole blood samples. These filtrates have been prepared in such a way that the concentration of non-protein-bound drug in the mixture is known exactly. Also, adding the blood to the ethanolic standard solution causes the protein to precipitate immediately, minimizing any loss of the anticoagulant due to reactions between the drugs and the unprecipitated protein. For the same reason, the mixture of the precipitate and the ethanolic supernatant liquid is centrifuged immediately after the mixture has been shaken sufficiently to ensure complete precipitation of the protein.

The background fluorescence and phosphorescence intensity signals due to the protein-free ethanolic filtrates of whole blood-bank samples were highly reproducible. The fluorimetric background signal was reproducible to $\pm 1\%$ on the second most sensitive scale of the photomultiplier microphotometer. The phosphorimetric

background signal due to the filtrate and ethanol was reproducible to ±10% on the same scale. The intensity signal of the phosphorimetric background, however, was notably smaller than that of the fluorimetric background. Consequently, slightly lower limiting detectable drug concentrations in the ethanol filtrate are obtainable by phosphorimetry than by fluorimetry when this procedure is used. These studies demonstrated that the blank luminescence backgrounds were insignificant at drug concentrations greater than 10 mg%.* At drug concentrations of 1 mg%, the luminescence background signal of the blank accounted for approximately 5% of the concentration. At 0·1 mg% concentration, the background signal due to the blank was significant and had to be considered in the calculations of the percentage of drug recovered.

In Table I, the fluorimetric and phosphorimetric excitation and emission wavelength peaks (uncorrected for instrumental response), the phosphorimetric decay times and phosphorimetric and fluorimetric limiting detectable concentrations for dicumarol, diphenadione, phenindione, tromexan and warfarin in ethanol are given. A comparison of the limiting detectable concentrations in Table I indicates that the fluorescence of warfarin is greater than that of the other anticoagulants. Except for warfarin, all of the anticoagulants used in this study had lower limiting detectable concentrations by phosphorimetric analysis than by fluorimetric analysis.

TABLE I.—FLUORESCENCE AND PHOSPHORESCENCE PARAMETERS OF SEVERAL ANTICOAGULANTS: WAVELENGTHS OF EMISSION AND EXCITATION PEAKS,* DECAY TIMES AND LIMITING DETECTABLE CONCENTRATIONS

	Fluorescence			Phosphorescence			
Anticoagulant	Excitation, λ, mμ	Emission, λ, mμ	L. of D.,‡ mg/ml	Excitation, λ, mμ	Emission, λ, mμ	Decay time, sec	L. of D.,‡ mg/ml
Dicumarol	370	435	0·01	305	455 475 (m)	0·6	0·001
Diphenadione	†	†	†	250, 260 (m),¶ 295	440 (m) 475	0·6	1·0
Phenindione	†	†	†	235 (m), 290	395	0·12	1·0
Tromexan	370	435	10	295 (m), 305	440, 460 (m)	0·6	0·01
Warfarin	320	390	0·001	305	460	0·8	0·01

* All wavelengths are uncorrected for instrumental characteristics.
† Fluorescence not analytically useful.
¶ (m) indicates the most intense peak.
‡ Limiting detectable concentration.

The intense fluorescence of warfarin permitted measurement over a fairly large concentration range without the need of special concentration procedures. Excellent recoveries of warfarin at relatively low concentrations in the prepared blood sample (0·1 mg%) were obtained by this procedure. The intense phosphorescence of dicumarol also allowed the measurement of this anticoagulant over a wide range of concentrations. In Table II typical recoveries of these two anticoagulants from the prepared whole blood samples are given. All data are averages of triplicate measurements on standards (at all three concentrations) and on blanks. Recoveries

* 1 mg% = 1 mg/100 ml of sample.

>90% were obtained at all three concentrations, for both drugs, when the protein-free ethanolic filtrates were used. The relative standard deviation on the three measurements of each concentration of each drug was <5% in all cases. Duplicate determinations of warfarin in blood samples can be made by fluorimetry in less than 15 min. It takes a little longer, however, by phosphorimetry because several more steps are needed in the measurement procedure.

TABLE II.—TYPICAL RECOVERIES OF WARFARIN BY FLUORESCENCE AND DICUMAROL BY PHOSPHORESCENCE*

Concentration, *mg %*	Amount recovered, *mg %*	Recovery, %
Warfarin		
10	9·8	98
1	0·95	95
0·1	0·093	93
Dicumarol		
10	9·7	97
1	0·92	92
0·1	0·095	95

* Each result represents the average of three determinations.

The advantages of the protein-free ethanolic filtrate for the fluorimetric and/or phosphorimetric analysis of whole blood samples are numerous. Several have been previously discussed in connection with the use of protein-free ethanolic filtrates of serum in the analysis of a number of sulpha drugs.[2] The advantages of using ethanol to deproteinize blood and as the solvent are: speed, ease of preparation, availability and low cost of solvent, low luminescent background, solubility of a large number of drugs, and the formation of a rigid clear glass at 77°K at a dilution of 1/20 (water: ethanol). It is important to note that there is no significant increase in the luminescence background signal of the protein-free ethanolic filtrates when whole blood is used in place of serum. It should also be noted that the ultimate advantage of using a protein-free ethanolic filtrate for analyses of drugs in blood, plasma or serum is that the compound of interest (in this case the anticoagulant) is separated from protein interferences, and the compound is diluted to volume in ethanol in the same step. There is then a low background when the anticoagulant in ethanol is measured directly by fluorimetry or phosphorimetry. No additional separation steps are necessary. When a non-protein-bound drug concentration is being measured the only possible loss is therefore adsorption of the drug on the surface of the precipitated protein. The same solution can be measured fluorimetrically and phosphorimetrically. Phenindione and diphenadione phosphoresce with fair sensitivity and do not fluoresce. The use of fluorimetry and phosphorimetry together should be useful for the analysis of mixtures of phenindione or diphenadione and any of the other fluorescing anticoagulants. This is possible because the fluorescing anticoagulants (especially dicumarol and warfarin) also phosphoresce. If such a mixture is first measured fluorimetrically, the concentration of the fluorescing species is determined without interference from the non-fluorescing species of the mixture (phenindione or diphenadione). Phosphorimetric analysis of the mixture yields a relative intensity

signal due to the phosphorescence of both components of the mixture. Because the concentration of one component is known from the fluorimetric analysis, the concentration of the second component is easily determined from the total phosphorescence signal.

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Résumé—On donne les maximums d'excitation et d'émission fluorimétriques et phosphorimétriques, les concentrations limites décelables et les temps d'affaiblissement phosphorimétrique pour la warfarine, le dicoumarol, la diphénandione, la phénindione et le tromexane. Des concentrations connues de warfarine, un composé fortement fluorescent, et de dicoumarol, un composé fortement phosphorescent, sont mesurées directement dans le système biochimique complexe du sang total. On a obtenu des récupérations excellentes en warfarine et dicoumarol dans le domaine de concentrations de 0,1 à 10 mg% dans le sang total.

Zusammenfassung—Anregungs- und Emissionsmaxima von Fluoreszenz und Phosphoreszenz sowie Nachweisgrenzen und Phosphoreszenzabklingdauern von Warfarin, Dicumarol, Diphenandion, Phenindion und Tromexan werden angegeben. Bekannte Konzentrationen von Warfarin, einer intensiv fluoreszierenden, und Dicumarol, einer stark phosphoreszierenden Substanz, wurden direkt in einem komplizierten biochemischen System, nämlich Vollblut, gemessen. Es wurden ausgezeichnete Ausbeuten an Warfarin und Dicumarol im Konzentrationsbereich 0,1 bis 10 mg-% in Vollblut erreicht.

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SUBSTOICHIOMETRIC SEPARATION IN ACTIVATION ANALYSIS

EXTRACTION OF CO-ORDINATIVELY-UNSOLVATED SALTS

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Summary—The necessary conditions have been examined for the use of extraction of coordinatively-unsolvated salts for substoichiometric separations in activation analysis, especially the influence of interfering ions and of the concentration of the carrier. A study has been made of the substoichiometric extraction of halide ions, oxyanions and anionic metal complexes by means of the tetraphenylarsonium ion into chloroform and dichloroethane, and of the extraction of alkali metal ions into nitrobenzene with tetraphenylborate. Substoichiometric extraction can be combined with neutron-activation analysis for the determination of traces of iodine, caesium, rubidium, manganese, rhenium, chromium, thallium, gold, gallium and tantalum.

NOT long ago, Růžička and Starý[1] suggested a new method of separation in activation analysis, called substoichiometric separation. For this purpose[2,3] the extraction of chelate compounds is very satisfactory, but it is limited to those metals which form stable chelates. The extraction of co-ordinatively unsolvated salts (*i.e.*, those containing large ions[4]) extends the range of the method, because the element to be determined can be present in either the cationic or the anionic part of the salt extracted.[5,6]

The necessary conditions for satisfactory substoichiometric separation by extraction of unsolvated salts can be derived in two ways if the ions in the salt have the same degree of charge. We can use the extraction constant K_{AB} for the system

$$A + B \rightleftharpoons (AB)_0; \qquad K_{AB} = [AB]_0/[A][B] \tag{1}$$

where $[AB]_0$ is the equilibrium concentration of the ion-pair $(AB)_0$ extracted into the organic phase, and [A] and [B] are the equilibrium concentrations of the two ions in the aqueous phase, and use it in conjunction with the initial concentrations of the reagent and the carrier of the element to be determined.[6] Alternatively, we can use the equations for the distribution ratio for the reagent, E_A,[5] which relate it to the original concentration of reagent C_A and carrier C_B,

$$E_A = K_{AB}[B] \approx K_{AB}(C_B - C_A) \tag{2}$$

and satisfy the requirement that at least 99% of the reagent added should be extracted,

$$E_A \geqslant 99\, v/v_0 \tag{3}$$

where v and v_0 are the volumes of the aqueous and organic phases respectively. Solution of equations (2) and (3) gives the value of the extraction constant:

$$\log K_{AB} \geqslant 2 + \log(v/v_0) - \log(C_B - C_A). \tag{4}$$

If the ions constituting the salt do not bear the same degree of charge, the conditions for substoichiometric separation to be satisfactory are more complicated.

It is understood that the roles of A and B may be reversed. The significance of the extraction constant K_{AB} depends on the size, charge and structure of the ions, the nature of the solvent, and on other factors.[4,7] The solvent must be little soluble in water, acid, or alkali, and must itself not be able to extract the element to be determined, unless the reagent is present.

TABLE I.—SOLUBILITY OF TETRAPHENYLARSONIUM SALTS IN CHLOROFORM AND 1,2-DICHLOROETHANE

Salt	Solubility, M	
	Chloroform	1,2-dichloroethane
$R_4AsAuCl_4$	$4{\cdot}4 \times 10^{-3}$	$>2{\cdot}8 \times 10^{-2}$
R_4AsReO_4	$1{\cdot}1 \times 10^{-3}$	$6{\cdot}1 \times 10^{-3}$
R_4AsMnO_4	$0{\cdot}7 \times 10^{-3}$	$3{\cdot}1 \times 10^{-3}$
R_4AsClO_4	$0{\cdot}8 \times 10^{-3}$	$1{\cdot}1 \times 10^{-2}$
R_4AsI	0·2	—
$(R_4As)_2Cr_2O_7$	—	$>3{\cdot}5 \times 10^{-2}$

Concentration of the carrier

In activation analysis, the concentration of carrier to be used is chosen arbitrarily. The upper limit is set by the solubility of the extracted species, and hence if $C_B = 2C_A$ the concentration of B is determined by the condition

$$C_B \leqslant 2S_{AB}v_0/v \tag{5}$$

where S_{AB} is the solubility of AB in the organic phase. In Table I the solubilities of some tetraphenylarsonium salts in chloroform and 1,2-dichloroethane are quoted.

The lower limit depends on K_{AB} and v/v_0; if $C_B = 2C_A$, then

$$\log C_B \geqslant 2{\cdot}3 + \log(v/v_0) - \log K_{AB}. \tag{6}$$

Thus rhenium(VII) for example, can be extracted substoichiometrically as its tetraphenylarsonium salt into chloroform over the concentration range $4 \times 10^{-4}M$ to $2 \times 10^{-3}M$ if $v = v_0$ and $C_B = 2C_A$. In principle, a specific amount of carrier can be isolated even when the rhenium concentration is less than $4 \times 10^{-4}M$, but the concentration of carrier must be controlled precisely, whereas at concentrations of rhenium carrier greater than $2 \times 10^{-4}M$ a change in the volume of the aqueous phase and loss of part of the carrier does not substantially influence the chemical yield. A wider range of carrier concentrations can be extracted with 1,2-dichloroethane ($a'b'$ in Fig. 1), and so this solvent is preferred.

The effect of interfering ions

Significant interference can be expected primarily from ions with the same charge as the carrier. The concentrations of the interfering ions (including any complexing ions) must not exceed a predetermined fraction of the concentrations of the reagent and of the carrier of the element to be determined, and can be derived by substituting

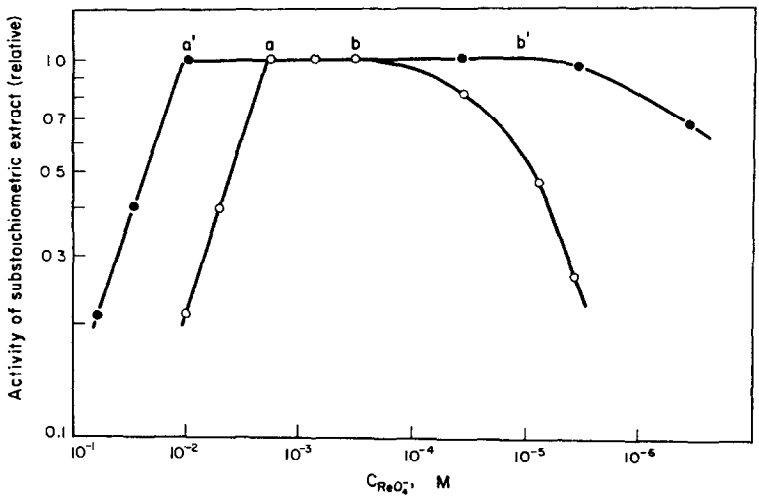

FIG. 1.—The influence of rhenium concentration on the substoichiometric extraction of perrhenate with tetraphenylarsonium chloride (50% stoichiometry).
○ with chloroform
● with 1,2-dichloroethane

the initial concentrations of the carrier and of the interfering ion (B′) into the ratio of the extraction constants for the two species:

$$\frac{K_{AB}}{K_{AB'}} = \frac{[AB]_0[B']}{[B][AB']_0}. \tag{7}$$

To maintain the condition of substoichiometric separation it is necessary that

$$[AB]_0 v_0 > 0{\cdot}99\, C_A v \tag{8}$$

$$[B]v < C_B v - 0{\cdot}99\, C_A v \tag{9}$$

$$[AB']_0 v_0 < 0{\cdot}01\, C_A v \tag{10}$$

$$[B']v > C_{B'} v - 0{\cdot}01\, C_A v. \tag{11}$$

By combining equations (7) to (11) we obtain the value for the threshold concentration of the interfering ion:

$$C_{B'} < 0{\cdot}01 \left[\frac{K_{AB} \cdot C_B}{K_{AB'} \cdot 0{\cdot}99} - \left(\frac{K_{AB}}{K_{AB'}} - 1 \right) C_A \right]. \tag{12}$$

If $C_B = 2C_A$, this simplifies to

$$C_{B'} < 0{\cdot}005 \left(\frac{K_{AB}}{K_{AB'}} + 1 \right) C_B. \tag{13}$$

It is obvious from equation (12) that if the carrier ion and the interfering ion have the same charge, then to give an adequate separation their exchange constant, *i.e.*,

$K_{AB}/K_{AB'}$, must be greater than 100. The exchange constant can be found experimentally from the equation:[8]

$$E_B = \frac{K_{AB}}{K_{AB'}} \cdot \frac{[AB']_0}{[B']} \tag{14}$$

where E_B is the distribution ratio of B when $C_B \ll C_A$ and $C_{B'} > C_A$.

In Fig. 2 the influence of chloride, nitrate, and perchlorate on the extraction of perrhenate as its tetraphenylarsonium salt into 1,2-dichloroethane is shown.

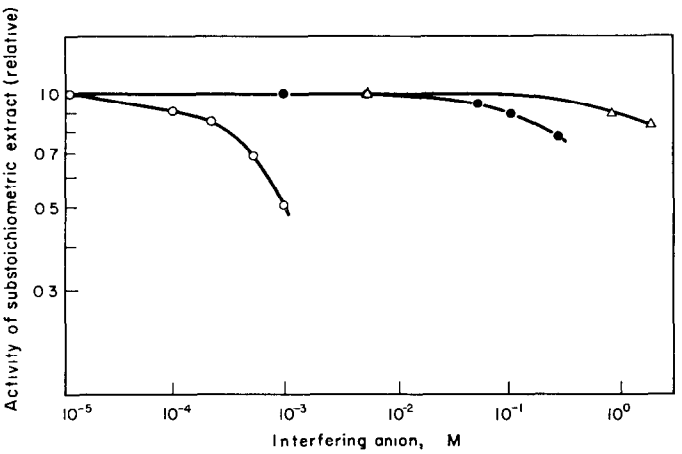

FIG. 2.—The influence of interfering anions on the substoichiometric extraction of rhenium(VII) with tetraphenylarsonium chloride into 1,2-dichloroethane ($10^{-3}M$ perrhenate, 50% stoichiometry).
○ perchlorate
● nitrate
△ chloride (chloroform extraction)

Selectivity

When co-ordinatively-unsolvated salts are extracted with an excess of the reagent, the distribution ratio is proportional to the extraction constant and the equilibrium concentration of the reagent in the aqueous phase:[8]

$$E_B = K_{AB}[A]$$

and

$$E_{B'} = K_{AB'}[A]. \tag{15}$$

If $K_{AB} > K_{AB'} \gg [A]^{-1}$ then both ions are being extracted quantitatively, and the degree of separation, β, is unity ($\beta = [AB]_0 C_{B'}/[AB']_0 C_B$). If, however, B is being extracted substoichiometrically, the degree of separation β_s will be much greater than unity; it can be shown that when $C_B = 2C_A$ and the conditions of equation (12) are fulfilled, then

$$\beta_s = (K_{AB} + K_{AB'})/2K_{AB'}. \tag{16}$$

It is seen that β_s changes from 1/2 when $K_{AB}/K_{AB'} \ll 1$, to $K_{AB}/2K_{AB'}$ when $K_{AB}/K_{AB'} \gg 1$.

SUBSTOICHIOMETRIC SEPARATIONS OF TETRAPHENYLARSONIUM SALTS

The extraction of large anions with tetraphenylarsonium cations (R_4As^+) as the reagent has been well studied. It is known[9] that ions such as I^-, NO_3^-, CN^-, SCN^-, MnO_4^-, TeO_4^-, ReO_4^-, ClO_3^-, ClO_4^-, and $Cr_2O_7^{2-}$ are easily extracted into chloroform with R_4As^+, whereas Br^-, Cl^-, BrO_3^-, IO_3^-, and IO_4^- are less well extracted, and the majority of the multi-charged oxyanions such as SO_4^{2-}, CrO_4^{2-}, MoO_4^{2-}, WO_4^{2-}, and PO_4^{3-} are very badly extracted. Examples are also known of the extraction of anionic

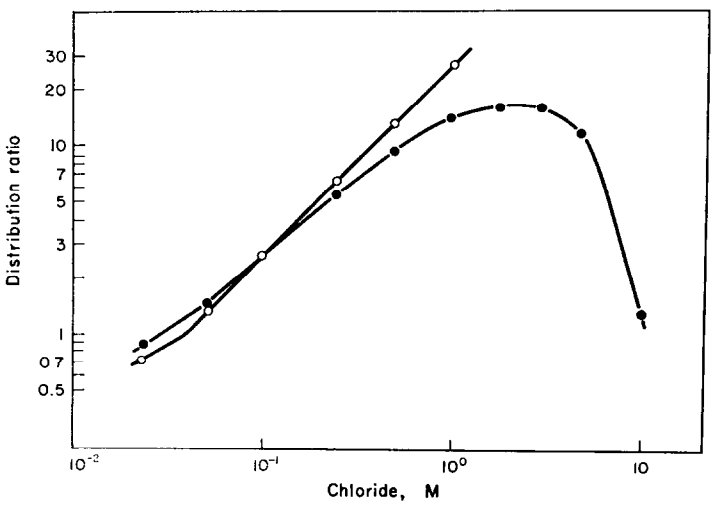

FIG. 3.—The influence of the concentration of potassium chloride and hydrochloric acid on the extraction of tetraphenylarsonium chloride with chloroform.
○ potassium chloride
● hydrochloric acid

metal complexes (halides, cyanides, thiocyanates, *etc.*) with R_4As^+ and other large cations. For example, Ueno[10] studied the extraction of 53 elements with tetraphenylarsonium chloride into chloroform from various concentrations of hydrochloric acid.

Halides

Tribalat[8] says the extraction constant of tetraphenylarsonium chloride into chloroform is 200. This value was obtained from the solubility of the reagent in water and chloroform. We have investigated the dependence of the distribution ratio of this reagent on the chloride concentration, the initial concentration of the reagent being $5 \times 10^{-4}M$ in the aqueous phase (Fig. 3). Over the range 0·045–0·9M potassium chloride there is a linear relationship with a slope of 30. In hydrochloric acid medium the distribution ratio passes through a maximum when the hydrochloric acid is about 3·5M. The distribution ratio for the reagent in the water-chloroform system is about 0·2 and is independent of pH over the range 0·1–12.[9]

In Table II results are given for the extraction of tetraphenylarsonium iodide from chloride or bromide solutions. The iodide distribution was determined radiometrically by means of ^{131}I. The exchange constants were calculated from equation

(14). It is clear that K_{R_4AsI} is much higher than K_{R_4AsCl} and K_{R_4AsBr} and that the difference is accentuated when 1,2-dichloroethane is used as solvent. The value of K_{R_4AsI} is about 10^5 for the chloroform system, and the extraction of iodide with a deficit of the tetraphenylarsonium reagent satisfies the conditions of equation (1) for substoichiometric separation if $v = v_0$ and $C_{I^-} > 2 \times 10^{-3}M$. The high solubility of tetraphenylarsonium iodide in chloroform (Table I) allows an iodide concentration higher than $10^{-2}M$ to be used. In this case the concentrations of bromide and chloride must not exceed $0{\cdot}01M$ and $0{\cdot}15M$ respectively [Table II and equation (13)].

TABLE II.—EXTRACTION OF ^{131}I FROM SOLUTIONS CONTAINING CHLORIDE OR BROMIDE AND SUBSTOICHIOMETRIC AMOUNTS OF TETRAPHENYLARSONIUM IONS

Solvent	Anion B′	Equilibrium concentration of B′ in the aqueous phase, M	Equilibrium concentration of R_4AsB' in the organic phase, M	Distribution ratio of iodide	Exchange constant
Chloroform	Cl^-	1·0	$1{\cdot}8 \times 10^{-3}$	5·4	3×10^3
	Br^-	0·2	$1{\cdot}5 \times 10^{-3}$	1·5	2×10^2
1,2-dichloroethane	Cl^-	1·0	$1{\cdot}8 \times 10^{-3}$	11	6×10^3

In an acidic medium there will be interference from metals such as bismuth, gold, mercury, *etc.*, which form anionic iodide complexes. The total concentration of such metals must not exceed $10^{-4}M$. Apparently the extraction constants of the R_4As^+ salts of these complexes (especially if they are singly-charged) are higher than the extraction constant for the iodide itself, and consequently trace quantities of these metals will be extracted quantitatively and may interfere radiometrically. The interference can be eliminated either by a preliminary conversion of the iodide into iodine which is then extracted with chloroform, or by a preliminary preferential extraction of the halo-complexes with an amount of R_4As^+ that is not more than a tenth of the amount to be used for extracting the iodide.

Oxyanions

In Table III are given results for the extraction of tetraphenylarsonium perrhenate into chloroform and 1,2-dichloroethane from solutions containing chloride, nitrate, thiocyanate, perchlorate, permanganate and dichromate. The distribution ratio of the rhenium was determined by means of ^{186}Re. Similar experiments were carried out with ^{99m}Tc from perrhenate solution. The exchange constants $K_{R_4AsTcO_4}/K_{R_4AsReO_4}$ were 1·7 and 2·5 for chloroform and 1,2-dichloroethane respectively.

The order of extractability into chloroform as tetraphenylarsonium salts is

$$MnO_4^- > TcO_4^- > ReO_4^- > ClO_4^- > (I^-, SCN^-, Cr_2O_7^{2-}) \gg NO_3^- > Br^- > Cl^-.$$

From Table III it is clear that manganese(VII), rhenium(VII), and chromium(VI) can be substoichiometrically separated by extraction of their tetraphenylarsonium salts into chloroform or 1,2-dichloroethane.

Manganese has been substoichiometrically separated after oxidation of manganese(II) to manganese(VII) by sodium bismuthate in sulphuric acid medium,

Table III.—Extraction of ^{186}Re from solution containing other anions and substoichiometric amounts of tetraphenylarsonium ions

Solvent	Anion B′	Equilibrium concentration of B′ in the aqueous phase, $M \times 10^3$	Equilibrium concentration of R_4As salt in the organic phase, $M \times 10^3$	Rhenium distribution ratio	Exchange constant
Chloroform	Cl^-	400*	0·28	8·0	$1·1 \times 10^4$
		800	0·30	3·9	$1·0 \times 10^4$
	NO_3^-	250	0·31	0·56	$4·5 \times 10^2$
		100	0·31	1·4	$4·5 \times 10^2$
	SCN^-	0·76	0·24	4·4	14
		2·76	0·24	1·3	15
	ClO_4^-	1·8	0·31	0·53	3·1
		3·9	0·31	0·25	3·1
	MnO_4^-	0·61	0·39	0·22	0·35
		0·81	0·195	0·09	0·37
	$Cr_2O_7^{2-}$	20	0·31	1·4†	—
1,2-dichloroethane	Cl^-	800	0·31	31	$8·0 \times 10^4$
		800	0·15	16	$8·5 \times 10^4$
	NO_3^-	500	0·39	1·0	$1·3 \times 10^3$
		250	0·39	2·1	$1·3 \times 10^3$
	SCN^-	1·8	0·24	3·3	25
		7·7	0·31	1·0	25
	ClO_4^-	0·67	0·39	0·58	1·0
		4·5	0·54	0·13	1·1
	MnO_4^-	0·61	0·39	0·1	0·16
		1·2	0·78	0·11	0·17
	$Cr_2O_7^{2-}$	20	0·31	0·95†	—

* That is, 0·4*M*.

† Determined in presence of 0·45*N* sulphuric acid (the distribution ratio increases with increase in pH).

following a preliminary separation of the manganese from interfering elements and reducing agents by precipitation as the hydroxide or manganese(IV) oxide.[11] Similar conditions are used for the separation of chromium(VI).

Technetium, formed by the reaction sequence $^{98}Mo(n,\gamma)^{99}Mo \xrightarrow{\beta} {}^{99m}Tc$, does not interfere with the substoichiometric separation of rhenium, because equation (13) always holds if the amount of technetium present is too small to be weighed, but ^{99m}Tc coextracted with rhenium (according to equation (16) and Table III) does interfere with measurement of ^{186}Re on a gamma-spectrometer because the γ-radiation energies of the two isotopes are very close (about 0·14 MeV).

The difference in redox potential of rhenium(VII) and technetium(VII) was made use of for their separation. In Fig. 4 is shown the effect of tin(II), added as sodium stannite, on the extraction of technetium and rhenium as their tetraphenylarsonium salts into chloroform or 1,2-dichloroethane from 0·3*M* sulphuric acid. A similar separation occurs from alkaline medium.

Anionic complexes of metals

Anions such as $AuCl_4^-$, $TlCl_4^-$, $FeCl_4^-$, $GaCl_4^-$ and $SbCl_6^-$, are easily extracted from hydrochloric acid solution as their R_4As^+ salts. Doubly-charged complex

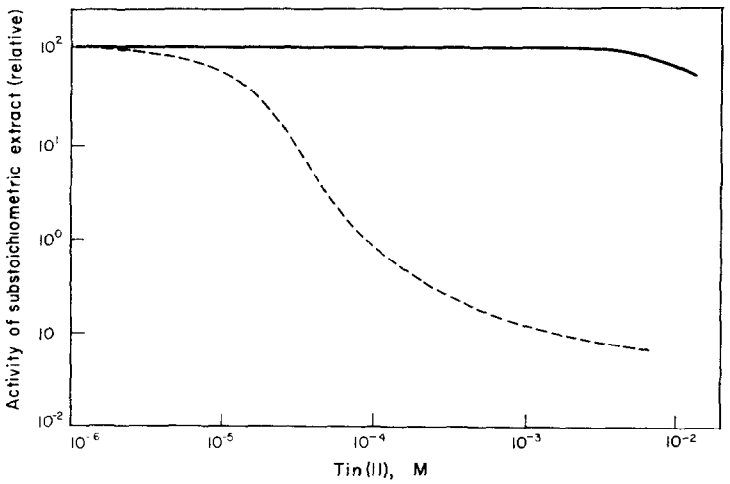

FIG. 4.—The influence of the tin(II) concentration on the substoichiometric extraction of tetraphenylarsonium perrhenate into 1,2-dichloroethane (50% stoichiometry).
— rhenium
--- coextraction of technetium

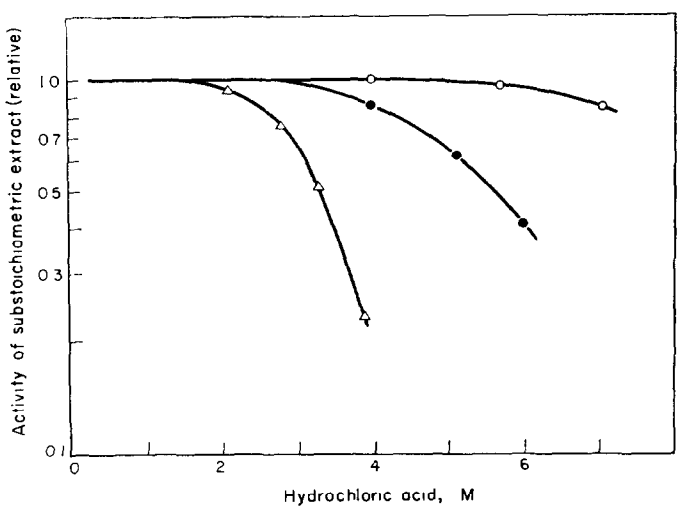

FIG. 5.—The influence of iron(III) and hydrochloric acid on the substoichiometric extraction of tetraphenylarsonium aurichloride into chloroform (50% stoichiometry).
○ Fe:Au 1:1
● Fe:Au 100:1
△ Fe:Au 1500:1

anions of this kind are very poorly extracted. The extent of formation of these ions depends markedly on the hydrochloric acid concentration, which explains why iron does not hinder the substoichiometric extraction of gold when the concentration of hydrochloric acid is $<1M$, even when the ratio of iron to gold is 1000:1 (Fig. 5).

In Table IV results are given for the extraction of tetraphenylarsonium tetrachloroaurate(III) into chloroform or 1,2-dichloroethane from solutions containing

TABLE IV.—EXTRACTION OF ^{198}Au FROM SOLUTIONS CONTAINING THALLIUM(III) OR IRON(III) CHLORO-COMPLEXES AND SUBSTOICHIOMETRIC AMOUNTS OF TETRAPHENYLARSONIUM IONS

Solvent	Anion B′	Equilibrium concentration of B′ in aqueous phase, $M \times 10^3$	Equilibrium concentration of R_4AsB' in organic phase, $M \times 10^3$	Distribution ratio of gold	Exchange constant
Chloroform	$TlCl_4^-$	0·48†	0·52	2·7	2·9
	$FeCl_4^-$*	44	0·54	0·08	6·6
		22	0·54	0·17	6·3
		22	1·4	0·43	6·5
1,2-dichloroethane	$TlCl_4^-$	0·48	0·52	0·94	1·0

* Determined in presence of $8M$ hydrochloric acid.
† That is $0{\cdot}48 \times 10^{-3}M$.

thallium(I) or iron(III). The distribution coefficient was determined by means of ^{198}Au. From Table IV it can be seen that the difference in the extraction constants is negligible. For the extraction of gold, the ratio $K_{R_4AsAuCl_4}/K_{R_4AsCl}$ is about $1{\cdot}5 \times 10^6$, *i.e.*, it is possible to separate gold, thallium, iron and gallium from hydrochloric acid solution substoichiometrically by this method.

TABLE V.—EXTRACTION OF ^{134}Cs INTO NITROBENZENE FROM SOLUTIONS CONTAINING OTHER ALKALI METALS AND SUBSTOICHIOMETRIC AMOUNTS OF TETRAPHENYLBORATE

Cation B′	Equilibrium concentration of B′ in the aqueous phase, $M \times 10^3$	Equilibrium concentration of R_4BB' in the organic phase, $M \times 10^3$	Distribution ratio of caesium	Exchange constant
Li^+	750*	0·9	13	$1{\cdot}1 \times 10^4$
	1500	0·9	6	1×10^4
Na^+	600	0·9	3·1	$2{\cdot}1 \times 10^3$
	1000	0·9	2·2	$2{\cdot}4 \times 10^3$
K^+	19	0·9	1·5	32
	200	0·9	0·16	35
Rb^+	19	0·9	0·32	6·8
	39	0·9	0·17	7·4
Tl^+	1·15	0·35	0·023	0·076
	0·65	0·35	0·040	0·074

* That is $0{\cdot}750M$.

The extraction of the anionic fluoride, bromide, iodide, cyanide and thiocyanate complexes is apparently suitable for the substoichiometric separation of such metals as tantalum, bismuth, molybdenum(V) and tungsten(V), sometimes with ions smaller than the tetraphenylarsonium ion. The thiocyanate complex of gold, for

example, can be extracted into 1,2-dichloroethane with the triphenylguanidine ion. Increase in the anionic radius, however, decreases the effect of anionic charge on selectivity of separation, and the permissible concentrations of complexing anions which themselves are easily extractable (such as iodide and thiocyanate) are limited according to equation (4).

SUBSTOICHIOMETRIC SEPARATIONS OF SIMPLE AND COMPLEX CATIONS

It is known that the alkali metal cations can be extracted into nitrobenzene as compounds with tetraphenylborate or dipicrylamine anions, or other large anions. Some results are given in Table V. The distribution coefficient was determined by means of ^{134}Cs. The extraction constant for caesium tetraphenylborate exceeds 10^6. It seems possible to separate thallium(I), caesium, rubidium, and possibly potassium, substoichiometrically by extraction of the tetraphenylborates. Small or multiply-charged cations are not extracted. Such ions may be extracted, however, in the form of their cationic complexes with certain chelating agents such as 2,2'-dipyridyl or 1,10-phenanthroline which form complexes with metals such as copper(I) and iron(II). In that case it is best to use as counter-ions large anions with the same degree of charge as the cation concerned.[7]

CONCLUSION

We have already used substoichiometric separation by extraction of coordinatively-unsolvated salts for the neutron activation determination of traces of gold[5] and manganese[11] in high purity metals, and of gold[12] and rhenium[13] in rocks and meteorites. This new method of separation of these elements in neutron activation analysis is much simpler and quicker than any used previously. The method seems extremely promising for the separation of iodine, caesium, rubidium, thallium, chromium, tantalum, and other metals.

Zusammenfassung—Die notwendigen Bedingungen zur Extraktion koordinativ nicht solvatisierter Salze zu unterstochiometrischen Trennungen in der Aktivierungsanalyse wurden untersucht, speziell der Einfluß störender Ionen und der Trägerkonzentration. Die unterstochiometrische Extraktion von Halogenidionen, Oxyanionen und anionischen Metallkomplexen mittels Tetraphenylarsoniumionen in Chloroform und Dichloräthan wurde studiert sowie die Extraktion von Alkalimetallionen mit Tetraphenyloborat in Nitrobenzol. Die unterstochiometrische Extraktion kann mit der Neutronenaktivierungsanalyse bei der Bestimmung von Spurenmengen Jod, Caesium, Rubidium, Mangan, Rhenium, Chrom, Thallium, Gold, Gallium und Tantal kombiniert werden.

Résumé—On a examiné les conditions qui sont nécessaires à l'usage de l'extraction de sels non solvatés par coordination pour les séparations substoechiométriques dans l'analyse par activation, essentiellement les influences des ions gênants et de la concentration du porteur. On a effectué une étude sur l'extraction substoechiométrique des ions halogénures, des oxyanions et des complexes métalliques anioniques au moyen d'ion tétraphénylarsonium en chloroforme et dichloréthane, et sur l'extraction des ions alcalins métaliques en nitrobenzène au moyen de tétraphénylborate. On peut combiner l'extraction substoechiométrique avec l'analyse par activation de neutrons pour le dosage de traces d'iode, caesium, rubidium, manganèse, rhénium, chrome, thallium, or, gallium et tantale.

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SHORT COMMUNICATIONS

Purification des colorants thiaziniques, Azur A, Azur B, Azur C, par une méthode de partage

(*Reçu le* 20 *Juil.* 1966. *Accepté le* 7 *Septembre* 1966)

LES méthodes de préparation des dérivés *N*-méthylés des colorants thiaziniques tel que l'Azur C (*N*-monométhyl thionine), l'Azur A (*N,N'*-diméthyl thionine) ou l'Azur B (*N,N'*-triméthyl thionine) conduisent inévitablement à des mélanges de thionines plus ou moins méthylés. La séparation des constituants du mélange est délicate car tous ces colorants ont pratiquement les mêmes propriétés physiques et chimiques et de plus, ils peuvent facilement perdre un ou plusieurs groupements méthyles.

Une méthode de séparation par chromatographie a été proposée par Taylor,[1] mais ce procédé met en jeu des solvants qui peuvent modifier la réactivité des colorants. Par ailleurs, elle n'est commode que pour séparer des quantités de colorants de l'ordre de la micromole.

A la suite d'une étude sur les propriétés acide-base des thiazines en milieu basique, nous avons remarqué qu'il était possible de séparer sélectivement ces colorants par une méthode de partage entre la solution aqueuse et un solvant organique non miscible à l'eau.

En solution aqueuse basique, la thionine et les azurs donnent lieu à un équilibre acide-base que l'on peut écrire de la façon suivante:

$$TH^+ + H_2O \rightleftharpoons T + H_3O^+$$

en désignant par TH^+ la forme ionique, et T la forme moléculaire du colorant. Nous avons déterminé, par spectroscopie, la constante de dissociation acide, $K_1 = [T][H^+]/[TH^+]$, de ces équilibres pour les différentes thionines et nous avons obtenu les résultats suivants:

	Thionine	Azur C	Azur A	Azur B
pK_1	11,0	11,5	11,8	12,1

La forme TH^+ est soluble dans l'eau et insoluble dans les solvants organiques non polaires alors que la forme moléculaire T se partage entre l'eau et les solvants organiques selon un équilibre de la forme $T_{aq} \rightleftarrows T_{org}$ dont la constante $K_2 = T_{org}/T_{aq}$ est d'autant plus grande que le colorant est plus méthylé. Le coefficient d'extraction K se met alors sous la forme:

$$K = \frac{[T_{org}]}{[T_{aq}] + [TH_{aq}^+]} = \frac{K_1 K_2}{K_1 + [H^+]}$$

A un pH donné, et pour un même solvant organique, ce coefficient dépend de la nature du colorant. Ainsi, en solution aqueuse tamponnée à pH 10 par un mélange d'acide acétique $10^{-2}M$, d'acide borique $10^{-2}M$, d'acide phosphorique $10^{-2}M$ et de soude en présence de tétrachlorure de carbone, nous avons mesuré les coefficients d'extraction suivants, à la température ambiante:

Thionine: 0,80 Azur A: 12

Azur C : 1,9 Azur B: 9,2

Ces valeurs permettent de calculer K_2 et le coefficient d'extraction pour d'autres valeurs du pH.

Le bleu de méthylène est le colorant le plus facile à éliminer d'un mélange de *N*-méthyl thionines car il n'a pas de forme moléculaire neutre. Lorsqu'on agite quelques minutes une solution de colorants, dont le pH est fixé à 11, en présence de tétrachlorure de carbone ou de benzene, le bleu de méthylène reste dans la phase aqueuse. Les azurs passent dans la phase organique sous leur forme moléculaire. Il est aisé par la suite de les reprendre par l'eau.

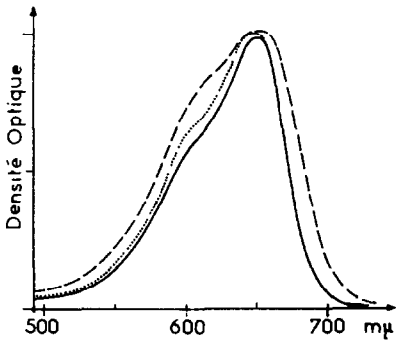

FIG. 1.—Azur B en solution aqueuse à pH 4,5.
– – – – Produit commerical
. . . . . Après un partage
————Après deux partages

En choisissant judicieusement le pH des solutions aqueuses et la phase à conserver après partage, on peut, suivant les cas, soit séparer les constituants d'un mélange d'azurs, soit purifier le colorant commercial.

Prenons par exemple, le cas de l'Azur B qui est généralement souillé de bleu de méthylène, d'Azur C et de thionine. Le spectre du colorant commercial dissous dans l'eau est donné sur la figure ci-jointe. Après un premier partage entre la solution aqueuse, dont le pH était initialement fixé à 10 par la soude, et du tétrachlorure de carbone, on obtient le spectre tracé en pointillé et après un deuxième partage, dans les mêmes conditions le spectre en trait plein.

En bon accord avec l'expérience, le calcul montre qu'après deux extractions le pourcentage d'Azur C, s'il était initialement de 10%, n'est plus que de 1%, le rendement en Azur B étant de 25%. Lorsque le taux d'impureté atteint cette valeur, les extractions suivantes ne modifient plus ni la forme de la bande, ni la position du maximum d'absorption.

En conclusion, le procédé de séparation des colorants thiaziniques par partage entre deux solvants non miscibles est rapide et satisfaisant lorsqu'il s'agit de purifier 10 à 20 micromoles de colorant. La purification de colorants en quantitiés plus importantes que celles auxquelles nous nous sommes interessés est encore possible, mais elle necessite la manipulation de volumes importants de solvant car solubilité des formes moléculaires est faible.

Enfin, il faut signaler que la solution aqueuse contient encore, outre le colorant, une certaine quantité de solvant non polaire. On peut l'éliminer par une filtration sur gel Sephadex.

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Résumé—On a séparé les uns des autres, ainsi que de la thionine et du bleu de méthylène, des dérivés N-méthylés de la thionine au moyen d'extraction en tétrachlorure de carbone à partir d'une solution aqueuse tamponnée au pH approprié pour chaque composé. On peut utiliser la méthode pour purifier les colorants.

Summary—Some *N*-methylated derivatives of thionine have been separated from thionine, Methylene Blue, and each other by solvent extraction into carbon tetrachloride from an aqueous solution buffered to the pH appropriate for each compound. The method can be used to purify the dyes.

Zusammenfassung—Einige N-methylierte Derivate von Thionin wurden von Thionin selbst, Methylenblau und untereinander durch Extraktion aus einer wäßrigen, am für die jeweilige Substanz geeigneten pH gepufferten Lösung in Tetrachlorkohlenstoff getrennt. Die Methode kann zur Reinigung der Farbstoffe dienen.

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Azo dyes from 2-amino-1,3,4-thiodiazole

(*Received* 7 *October* 1966. *Accepted* 9 *October* 1966)

2-AMINO-1,3,4-THIODIAZOLE is similar to 2-aminothiazole, in that it can be diazotized with nitrous acid.[1] The colorimetric properties of the thiodiazolylazo dyes have not been studied except for the β-naphthol compound which has been used as an acid-base indicator.[2] Substituted thiodiazolylazo compounds have also been investigated both academically and as commercial dyestuffs.[3,4]

EXPERIMENTAL

Preparation of reagents

Thiosemicarbazide was treated with formic acid to give 2-formamido-1,3,4-thiodiazole,[5] which was then heated with hydrochloric acid to produce the amine. 2-Amino-1,3,4-thiodiazole was more water-soluble than 2-aminothiazole but on diazotization gave lower yields of the dyestuffs. Thiodiazolylazo dyes from resorcinol (TdAR), *p*-cresol (TdA*p*C) and β-naphthol (TdANβ) were prepared.

RESULTS AND DISCUSSION

TdAR is a yellow dye, orange in alkali, which gives red-brown complexes with many metal ions. TdA*p*C was very similar to thiazolylazo-*p*-cresol (TA*p*C) giving colour changes from yellow to blue on chelation, whereas TdANβ was paler than thiazolylazo-β-naphthol (TANβ). These three thiodiazolylazo dyes all gave greenish complexes with iron and ruthenium. TdAR, TdANβ, and TdA*p*C were not obtained in a very pure state, but were definitely less sensitive towards all metals than the thiazolylazo dyes. This is probably due to the lower basicity of the nitrogen atom of the thiodiazole ring. In a similar manner, the extra nitrogen atom present in 8-hydroxycinnoline causes it to form weaker complexes than 8-hydroxyquinoline.[6] Since the thiodiazolylazo dyes also produce duller colour changes than their thiazole and triazole analogues, they were inferior in all respects.

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Summary—Thiodiazolyazo dyes from resorcinol, *p*-cresol and β-naphthol have been prepared. They are inferior to their thiazole and triazole analogues in their colour-forming reactions with metal ions.

Résumé—On a préparé les colorants thiodiazolylazo du résorcinol, du *p*-crésol et du β-naphtol. Dans leurs réactions colorées avec les ions métalliques, ils sont inférieurs à leurs analogues thiazoliques et triazoliques.

Zusammenfassung—Es wurden Thiodiazolylazofarbstoffe von Resorcin, *p*-Kresol und β-Naphthol hergestellt. Sie sind in ihren farbbildenden Reaktionen mit Metallionen ihren Thiazol- und Triazolanalogen unterlegen.

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Semimicro method for the determination of linalol in coriander oil

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THE determination of linalol is a problem in the analysis of essential oils. The methods used are those suggested for the determination of tertiary alcohols. These determinations require from 6 hr to 4 days[1] for their completion and involve the use of special reagents.[2,3] In addition, large samples (10 g) are needed. Semimicro methods[4] and colorimetric methods[5] also need special reagents and apparatus.

Linalol gives a green colour when sodium nitrite solution and hydrochloric acid are added to the essential oil that contains it.[6] This reaction can be used for the determination of linalol.

EXPERIMENTAL

Reagents

Linalol was obtained from coriander oil by saponification with 10% potassium hydroxide solution. The product was redistilled three times under reduced pressure (13 mm Hg). The gas chromatogram indicated a purity of 99·5%. It had the following properties:

$$n_D^{20} = 1{\cdot}4629, \quad \alpha_D^{20} = 11{\cdot}5°, \quad d_{20}^{20} = 0{\cdot}8679, \quad \text{b.p.} = 84\text{–}86°/13 \text{ mm}$$

Aqueous sodium nitrate solution, 50%.
Hydrochloric acid, 25%.
Anhydrous sodium sulphate, dried at 200°.

Specificity of the reaction

Gorjaev and Pliva[6] recommend this reaction for qualitative identification of linalol in essential oils, but we find that other compounds give the same colour. Table I shows the results obtained by treating toluene solutions of the most common components of essential oils with sodium nitrite and hydrochloric acid.

TABLE I.—REACTION OF SOME COMPONENTS OF ESSENTIAL OILS WITH NITROUS ACID

Compound	Colour produced	Compound	Colour produced
Linalol	green	Eugenol	none
Linalol acetate	green	Borneol	none
Geraniol	green	Menthol	none
Geraniol acetate	green	Menthone	none
Dipentene	green	Menthol acetate	none
Terpineol	green	α-Pinene	none
Terpineol acetate	green	β-Pinene	none
Citronellol	green	Δ^3-Carene	none
Citronellal	green	Hydroxycitronellal	none
Nerol	green	Sclareol	none
Indole	red	Ionone	none
Nonyl alcohol	none	Thymol	none
Decyl alcohol	none	Anethole	none
		Vanillin	none

Standardisation

A stock solution of linalol was prepared by dissolving 4 g of it in 100 ml of toluene. Different volumes of this solution (0–5·00 ml) were diluted with toluene to 5·00 ml. To each solution was added 1·00 ml of sodium nitrite solution and 1·00 ml of hydrochloric acid. The mixtures were shaken for 5–10 sec and left in the dark for 1–2 min. When reaction was complete (3 min) the toluene layer was separated and 2–3 g of sodium sulphate were added. After 3 min, the toluene was decanted, and its absorbance against a reagent blank was measured at 680 nm. The absorption spectrum of the solution is shown in Fig. 1(a), and a calibration curve in Fig. 1(b).

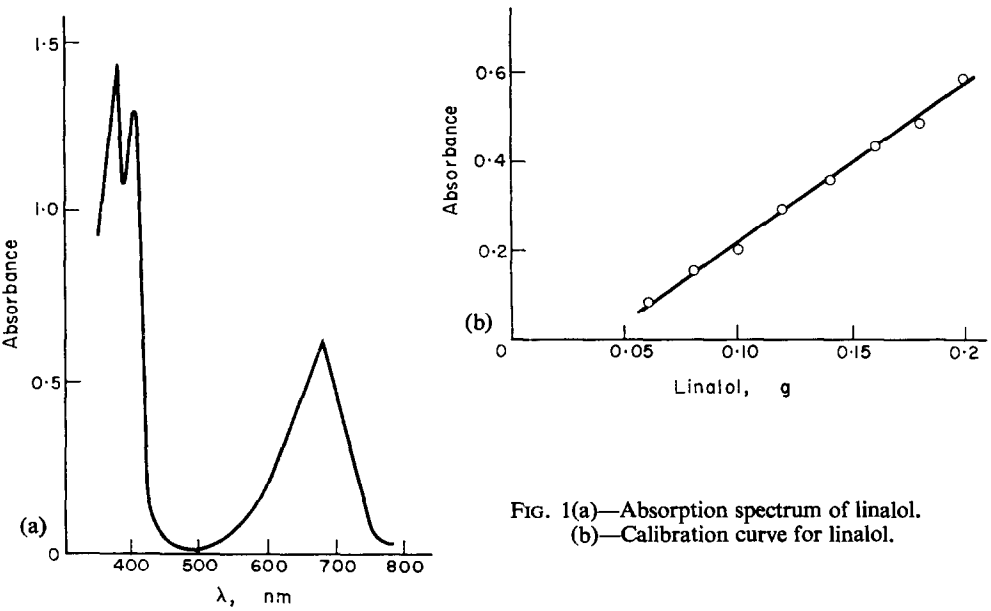

FIG. 1(a)—Absorption spectrum of linalol.
(b)—Calibration curve for linalol.

Procedure

A sample of 0·15–0·2 g of essential oil was dissolved in 5 ml of toluene, and treated as described under *Standardisation*. Different quantities of rectified and raw coriander oil were analysed. The results are given in Tables II and III.

TABLE II.—RECTIFIED CORIANDER OIL

Oil,	Linalol found,		Deviation from mean,
g	*g*	%	%
0·1277	0·1120	87·8	−0·8
0·1287	0·1152	90·3	+0·7
0·1547	0·1375	89·0	+0·4
0·1737	0·1530	89·2	+0·6
0·1787	0·1550	87·0	−1·6

TABLE III.—RAW CORIANDER OIL

Oil,	Linalol found,		Deviation from mean,
g	*g*	%	%
0·1257	0·0785	62·5	−0·4
0·1300	0·0847	65·2	+2·3
0·1682	0·1045	62·3	−0·6
0·1699	0·1045	61·6	−1·3

DISCUSSION

Coriander oil contains mainly linalol and linalol acetate. Gerianol acetate and dipentene are present in low concentration.[7] By this method all compounds giving a green colour are calculated as linalol. The green colour is photo-sensitive but persists in the dark for several days. Pure benzene and toluene also give an initial green colour but this fades rapidly, and does not interfere with determinations made after 5 min.

The amount of nitrous acid is critical for the determination. The hydroxyl group is not involved in the formation of the green compound, since acetates also give a green colour. In order to verify this we analysed coriander oil and its esterified products. Samples were formylated by the method of Glichitch and acetylated by the standard method.[8] The method adopted by British Standards[9] and

the Holness procedure[10] are better than the Grasse method but we preferred the latter in order to establish whether the dehydration hinders the determination of linalol. All three products were analysed, and the quantity of linalol calculated. The results (Table IV) show that the formylated and acetylated oils contain almost the theoretical quantities of linalol. The dehydration which takes place during the esterification does not hinder the determination.

TABLE IV.—ANALYSIS OF THE ESTERIFIED ESSENTIAL OILS

	Linalol, %	
	found	theoretical
After formylation	75·5	76·1
	75·0	76·1
After acetylation	71·0	71·3
	72·2	71·3

CONCLUSION

The new method is rapid and requires very small quantities of the essential oil. The reaction is not specific for linalol but if other active components are present in low concentration the results are satisfactory. The error is lower than that for the method of Glichitch provided that the absorbance lies in the range 0·15–0·45.

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Summary—Linalol has been determined colorimetrically in essential oils by means of the green colour developed in the presence of nitrous acid. Geraniol, dipentene, terpineol, citronellol and citral also give a green colour, and are therefore calculated as linalol by this method, but the error is small if they are present in small concentrations.

Zusammenfassung—Linalool wurde in ätherischen Ölen mit Hilfe der grünen Farbe, die es in Gegenwart salpetriger Säure entwickelt, kolorimetrisch bestimmt. Geraniol, Dipenten, Terpineol, Citronellol und Citral geben auch eine grüne Farbe und werden deshalb bei dieser Methode als Linalool mitberechnet, aber der Fehler ist gering, wenn sie in geringen Konzentrationen vorhanden sind.

Résumé—On a dosé colorimétriquement le linalol dans les huiles essentielles au moyen de la coloration verte qu'il développe en présence d'acide nitreux. Le géraniol, le dipentène, le terpinéol, le citronellol et le citral donnent également une coloration verte et sont par conséquent calculés en tant que linalol par cette méthode, mais l'erreur est petite s'ils sont présents à de faibles concentrations.

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Photo-induced oxidation of some organic carbonyl compounds by vanadium(V)

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WE have previously described[1-6] some applications of vanadium(V) in quantitative organic analysis. These oxidation reactions are slow at room temperature and require heating, with resultant loss of the more volatile organic substances. Renz[7] reported in 1921 that mixtures of vanadium(V) and some organic substances are photo-sensitive and that on exposure to sunlight carbon dioxide is evolved, but no quantitative examination of these reactions has been recorded. We have now observed that oxidation of several carbonyl compounds with vanadium(V) may be effected smoothly and rapidly at room temperature by illuminating the reaction mixtures with visible light. The reactions are quantitative and stoichiometrically resemble these effected by heating.

EXPERIMENTAL

Reagents

Vanadium(V) solution, 0·1*N*. The required amount of sodium metavanadate (Merck) was dissolved in the minimum of sulphuric acid necessary, and diluted to the required volume. The solution was standardized with a standard iron(II) solution, *N*-phenylanthranilic acid being used as indicator.

Carbonyl compounds. Pyruvic and levulinic acid solutions, 0·01*M*, were prepared by appropriate dilution of more concentrated solutions that had been standardized alkalimetrically. The solutions were checked by a permanganate titration. Acetaldehyde solution, 0·2*M*, was prepared, standardized iodometrically, and diluted to 0·05*M*. Isobutyraldehyde, crotonaldehyde and acetylacetone solutions, 0·01*M*, were prepared by diluting the pure reagent to the volume required.

Procedure

The reaction mixtures consisted of an aliquot of vanadate solution containing sufficient sulphuric acid to give the desired final acid concentration, and an aliquot of the solution of the compound under study, diluted to a total volume of 50 ml. The reaction vessels were 250-ml pyrex iodine flasks.

The reaction mixtures were exposed to the radiation of a 1000-W tungsten-filament lamp at a distance of about 18 in. At intervals of time, the mixtures were diluted and titrated with standard iron(II) solution to determine the amount of oxidant consumed. A constant minimum consumption of iron(II) solution was taken as indication of the completion of the reaction. A blank was run simultaneously.

The oxidation was studied at different total concentrations of the oxidant (0·01–0·08*N*), sulphuric acid (5·4–9*F*) and the organic compound (0·001–0·0005*M*) and the optimum conditions were found for the quantitative oxidation.

RESULTS

In Table I are presented the results obtained under optimum conditions. Pyruvic acid reacts much faster than the other compounds tested.

TABLE I

Reaction mixture			Consumption of vanadate, *eq/mole*	Time needed to complete reaction, *min*
Sample, *ml*	Vanadate, *ml*	Conc. sulphuric acid, *ml*		
0·01*M* Pyruvic acid, 5	0·01*N*, 20	15	2·00	10
0·01*M* Levulinic acid, 5	0·2*N*, 20	25	12·0	40
0·05*M* Acetaldehyde, 3·5	0·2*N*, 20	25	8·05	30
0·01*M* Isobutyraldehyde, 5	0·2*N*, 20	25	4·00	120
0·01*M* Crotonaldehyde, 2·5	0·1*N*, 20	20	10·0	30
0·01*M* Acetylacetone, 5	0·1*N*, 20	30	7·95	30

DISCUSSION

Pyruvic acid undergoes fast oxidation with acid vanadate solution, consuming 2 equivalents of the oxidant per mole of acid. This suggests that pyruvic acid is oxidized to acetic acid directly, without intermediate formation of acetaldehyde, which would cause a higher consumption of oxidant (see below). Probably the absence of hydrogen on the α-carbon atom in pyruvic acid prevents the formation of acetaldehyde and is also responsible for the fast oxidation. The method gives quite accurate results and can be used to estimate pyruvic acid in the presence of formic and acetic acids.

The oxidation of levulinic acid, a γ-keto acid, is slower than that of an α-keto acid. The 12 equivalents of oxidant consumed per mole of acid suggest that during oxidation a mole each of formic and acetic acids and water are formed, with evolution of two moles of carbon dioxide. Thus a molecule of levulinic acid is probably first oxidized to a molecule each of acetic and malonic acids. The former resists further oxidation whereas the latter readily undergoes oxidation to formic acid, carbon dioxide and water. This view is supported by the fact that 6 equivalents of oxidant are consumed per mole of malonic acid, in agreement with the proposed mechanism.

The results for the oxidation of acetaldehyde indicate that the oxidation does not yield acetic acid. Probably the aldehyde undergoes enolization followed by hydroxylation of the double bond, which promotes further oxidation to give formic acid as the end product. The mechanism of the reaction has been discussed earlier.[5]

Isobutyraldehyde undergoes slower oxidation than acetaldehyde, consuming 4 equivalents of the oxidant per mole of the aldehyde. This suggests that the oxidation takes place with the formation of a molecule each of acetone and formic acid, in agreement with the observations of Jones and Waters.[8]

Acetylacetone and crotonaldehyde consume 8 and 10 equivalents, respectively, of the oxidant per mole of the compound, which suggests the formation of a mole each of acetic and formic acids and carbon dioxide in the case of crotonaldehyde and two moles of acetic acid and a mole of carbon dioxide with acetylacetone.

All this suggests that during oxidation C—C bond fission takes place. Such oxidations, involving the elimination of a carbon atom should proceed by enolization followed by hydroxylation of the double bond so produced. The hydroxylated product then undergoes oxidation resulting in C—C bond cleavage. The fact that the overall reaction is facilitated by an increase in acid concentration supports these conclusions, as the intermediate steps are known to be acid catalysed.[9] These observations are in good agreement with those of Jones and Waters, who have demonstrated that C—C bond fission occurs in oxidations with vanadium(V).[10]

The presence of various end-products in the reaction mixture after completion of oxidation was confirmed by qualitative tests. A quantitative determination was, however, not always successful, *e.g.*, recovery of formic acid never exceeded 50%, probably because of decomposition in the presence of conc. sulphuric acid, and the recovery of carbon dioxide and acetic acid was only about 90%.

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Summary—The oxidation of pyruvic acid, levulinic acid, acetaldehyde, isobutyraldehyde and acetylacetone by vanadium(V) in aqueous solution on illumination with visible light is described. Pyruvic acid undergoes oxidation much more rapidly than does levulinic acid; both give acetic acid. Acetaldehyde is more rapidly oxidized than is isobutyraldehyde, the former giving formic acid, and the latter, formic acid and acetone. Acetylacetone is converted into acetic acid. The oxidations are rapid and quantitative and may be used for the estimation of these carbonyl compounds.

Résumé—On décrit l'oxydation de l'acide pyruvique, de l'acide lévulinique, de l'acétaldéhyde, de l'isobutyraldéhyde et de l'acétylacétone par le vanadium (V), en solution aqueuse irradiée en lumière visible. L'acide pyruvique subit l'oxydation beaucoup plus rapidement que l'acide lévulinique; tous deux fournissent de l'acide acétique. L'acétaldéhyde s'oxyde plus rapidement que l'isobutyraldéhyde, le premier donnant de l'acide formique et le second de l'acide formique et de l'acétone. L'acétylacétone est convertie en acide acétique. Les oxydations sont rapides et quantitatives et l'on peut les utiliser pour l'estimation de ces composés carbonylés.

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Zusammenfassung—Die Oxydation von Brenztrauben- und Lävulinsäure, Acetaldehyd, Isobutyraldehyd und Acetylaceton durch Vanadium(V) in wäßriger Lösung bei Bestrahlung mit sichtbarem Licht wird beschrieben. Brenztraubensäure wird viel schneller oxydiert als Lävulinsäure; beide liefern Essigsäure. Acetaldehyd wird schneller als Isobutyraldehyd oxydiert; ersterer bildet Ameisensäure, letzterer Ameisensäure und Aceton. Acetylaceton gibt Essigsäure als Produkt. Die Oxydationen gehen schnell und quantitativ und können zur Bestimmung dieser Carbonylverbindungen herangezogen werden.

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Amalgam exchange separation of radiothallium

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AMALGAM exchange is a rapid and selective method which may be used for the separation of various elements. Although this technique was first used in 1936 by Lewis and McDonald[1] for enriching lithium isotopes, only recently has it been applied to the radiochemical separation of various elements. The method has been used for the radiochemical separation of cadmium,[2] zinc[3] and indium.[4] Limited studies on the amalgam exchange of strontium and thallium have also been reported.[5] The procedure developed in this investigation is rapid and selective and may be used to separate short-lived isotopes such as thallium-202, and determine their activities.

EXPERIMENTAL

Apparatus

Standard radiochemical equipment was used throughout this work. Beta-activity of thallium-204 was counted with an end-window Geiger tube of the halogen-quenched type which was mounted in a vertical lead shield.

Reagents

Thallium-204 was obtained from the Isotopes Division of Oak Ridge National Laboratory. The desired activity was obtained by dilution of the tracer with 0·1*M* nitric acid.

Ethylenediamine, 85% solution in water.

Mercury, reagent-grade (base metals 1×10^{-4}%, foreign metals 5×10^{-4}%).

Nitrogen gas, water-pumped, stored in tank.

Thallium metal, 99+%, Amend Drug and Chemical Co., New York.

Thallium amalgam, 3%; 0·88 g of thallium metal was cleaned with 0·1*M* nitric acid and mixed with 2 ml (27·2 g) of mercury in a test-tube. The amalgam was kept under distilled water and oxygen was removed from the system by purging with nitrogen.

Preliminary experiments

Radiothallium solution was mixed with various reagents, flushed with nitrogen to remove oxygen

Zusammenfassung—Die Oxydation von Brenztrauben- und Lävulinsäure, Acetaldehyd, Isobutyraldehyd und Acetylaceton durch Vanadium(V) in wäßriger Lösung bei Bestrahlung mit sichtbarem Licht wird beschrieben. Brenztraubensäure wird viel schneller oxydiert als Lävulinsäure; beide liefern Essigsäure. Acetaldehyd wird schneller als Isobutyraldehyd oxydiert; ersterer bildet Ameisensäure, letzterer Ameisensäure und Aceton. Acetylaceton gibt Essigsäure als Produkt. Die Oxydationen gehen schnell und quantitativ und können zur Bestimmung dieser Carbonylverbindungen herangezogen werden.

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Preliminary experiments

Radiothallium solution was mixed with various reagents, flushed with nitrogen to remove oxygen

and then shaken with thallium amalgam. Portions of the aqueous phase were than removed and their activity measured to determine the amount of exchange that had occurred. The amalgam phase was then separated and shaken with a back-extractant, and the amount of radiothallium extracted into the aqueous phase was measured by counting its activity. Anions, complexing agents and pH exert definite effects on the efficiency of the exchange steps. Several anions and complexing agents were investigated to obtain maximum efficiency in the amalgamation step. Fluoride, nitrate, sulphate and perchlorate were the anions investigated. Ethylenediamine (EDA), triethanolamine (TEA), phenylethylamine (PEA), EDTA, hyamine perchlorate and ammonia were tried as complexing agents. The results of this investigation are summarized in Table I. The degree of exchange observed in the presence of PEA, TEA, and EDA is almost identical. Hyamine perchlorate inhibits the exchange step. The ethylenediamine and fluoride systems were selected for extensive study.

TABLE I

Anion or complexing agent	^{204}Tl added, *cpm*	Total activity in aqueous phase *cpm*	Exchange into the amalgam, %
0·1*M* Hyamine perchlorate	22450	20500	8·5
PEA, 2·5%	22450	1350	94·0
TEA, 2·5%	22450	1335	94·0
EDA, 2·5%	22450	1360	93·9
0·1*M* EDTA	22450	2980	86·7
0·25*M* Ammonia	22450	3475	84·6
0·25*M* Fluoride	8890	336	96·2
0·25*M* Sulphate	8890	1323	85·1
0·25*M* Perchlorate	8890	567	93·6
0·25*M* Nitrate	8890	600	93·2

It was found that dilution of the amalgam by the addition of 1 ml of mercury to 100 μl of amalgam increases the efficiency considerably. With undiluted amalgam, the back-extraction step had an efficiency of approximately 20%, but with the diluted amalgam the efficiency rose to 97%. Various acids were studied in the back-extraction. A summary of this investigation is given in Table II.

TABLE II.—EFFECT OF VARIOUS ACIDS ON BACK-EXTRACTION

Exchange system	^{204}Tl exchanged into amalgam, %	Back-extractant	^{204}Tl back-extracted into amalgam, %
500 μl tracer + 100 μl EDA + 100 μl 3% amalgam + 500 μl 0·1*M* NH_4OH	91·7 92·2	Co^{2+}, 2 ml Co^{2+}, 2 ml + 1 ml 6*M* HCl	21·7 16·0
500 μl tracer + 200 μl EDA + 500 μl 0·1*M* NH_4OH + 200 μl 3% amalgam	93·2 92·9 93·5	Co^{2+}, 2 ml + 2 ml 0·5*M* HNO_3 Co^{2+}, 2 ml + 1 ml 1*M* CH_3COOH Co^{2+}, 2 ml + 1 ml 1*M* $HClO_4$	19·0 20·2 13·7
Amalgam diluted with 1 ml of mercury before back-extraction			
500 μl tracer + 200 μl EDA + 500 μl 0·1*M* NH_4OH + 200 μl 3% amalgam	92·9 93·2 93·7	Co^{2+}, 2 ml + 1 ml 1*M* $HClO_4$ Co^{2+}, 2 ml + 1 ml 0·5*M* HNO- Co^{2+}, 2 ml + 1 ml 1*M* CH_3COOH	88·7 97·0 97·3

The effect of pH on the amalgamation step was studied and a summary of the results is given in Table III. It is observed that the exchange is not greatly affected by the change in pH except when nitric acid is present. In this case, it is possible that the thallium in the amalgam is oxidized by the nitric acid and extracted, and so the efficiency of isotopic exchange is lowered. A pH above 3 is preferred.

TABLE III.—EFFECT OF pH

System	pH	Exchange into amalgam, %
200 μl tracer + 100 μl 3% amalgam		
1 ml 4M HNO_3 + 3 ml 1M NaF	0	88·7
1 ml 0·4M HNO_3 + 3 ml 1M NaF	1	93·6
3 ml 1M NaF + 1 ml H_2O + 0·1M NH_4OH	3	96·7
3 ml 1M NaF + 1 ml H_2O + 0·1M NH_4OH	4	96·3
3 ml 1M NaF + 1 ml H_2O + 0·1M NH_4OH	7	97·6
3 ml 1M NaF + 1 ml H_2O + 1 ml 0·5M NH_4OH	11·2	96·4

TABLE IV.—EFFICIENCY OF PROCEDURE

Complexing agent	Amount exchanged into amalgam, %	Amount extracted from diluted amalgam, %	Overall recovery, %
EDA, 0·21%	93·5 ± 1·4	96·0 ± 1·1	89·6 ± 1·6*
Fluoride, 0·25M	94·3 ± 1·4	94·8 ± 0·5	89·3 ± 1·1†

Errors quoted are standard deviations
* Average of 8 experiments
† Average of 9 experiments

Amalgam exchange procedure for thallium-204

On the basis of the preceding studies, the following procedure was devised for the amalgam exchange separation of thallium-204.

Amalgam exchange step: 500 μl of thallium-204 tracer were mixed with 500 μl of 0·1M ammonia in a test-tube, and 100 μl of 85% ethylenediamine or 3 ml of 1M sodium fluoride were added. If EDA was added, the solution was diluted to 4·0 ml with distilled water. Nitrogen was passed through the sample to remove oxygen. Then 100 μl of freshly prepared 3% amalgam were added, and the test-tube was stoppered tightly and shaken vigorously for 5 min. Then 500 μl of the supernatant liquid were transferred to a planchette, dried and counted for 5 min. The per cent activity exchanged into the amalgam was calculated. A standard was also counted under the same conditions.

Back-extraction step: the supernatant liquid was removed by syringe micro-pipette and the amalgam was washed with 1 ml of distilled water. The amalgam was dried with a Kleenex tissue and the amalgam bead transferred into another test-tube containing 1 ml of mercury, 3 ml of cobalt nitrate solution (50 mg of Co/ml) and 1 ml of 0·5M nitric acid. The diluted amalgam was shaken with the aqueous solution for 4 min. The supernatant liquid was transferred into a fresh test-tube and the amalgam was washed with 1 ml of 0·1M nitric acid which was then added to the aqueous phase already separated; 500 μl of this solution were transferred to a planchette, dried and counted for 5 min. For short-lived isotopes, a shorter mixing time may be chosen. The efficiencies of extraction from the amalgam and of overall separation were calculated.

RESULTS

The procedure with ethylenediamine and sodium fluoride as the complexing agents was carried through and the results are given in Table IV.

The minimum time needed for this procedure is about 7 min and the recoveries are about 90%. This procedure, therefore, satisfies the need for a rapid, efficient and simple radiochemical separation for thallium isotopes.

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Summary—A method is presented for the rapid separation of radiothallium. The solution is made basic by addition of ammonia, then sodium fluoride and ethylenediamine are added and the mixture is shaken with 3% thallium amalgam. A rapid exchange takes place and the bulk of the activity is concentrated in the amalgam. The amalgam is diluted with clean mercury and shaken with acidic cobalt nitrate solution which back-extracts thallium. About 90% of the thallium activity is recovered.

Résumé—On présente une méthode pour la séparation rapide du radiothallium. La solution est alcalinisée par addition d'ammoniaque, puis on ajoute du fluorure de sodium et de l'éthylènediamine et agite le mélange avec de l'amalgame de thallium à 3%. Il se produit un échange rapide et la majeure partie de l'activité est concentrée dans l'amalgame. On dilue l'amalgame au moyen de mercure propre et l'agite avec une solution acide de nitrate de cobalt qui réextrait le thallium. On récupère environ 90% de l'activité du thallium.

Zusammenfassung—Ein Verfahren zur schnellen Abtrennung von Radiothallium wird angegeben. Die Lösung wird durch Ammoniakzusatz basisch gemacht, Natriumfluorid und Äthylendiamin zugesetzt und mit 3%-igem Thalliumamalgam geschüttelt. Es findet ein rascher Austausch statt, nach dem der Hauptteil der Aktivität sich im Amalgam befindet. Das Amalgam wird mit reinem Quecksilber verdünnt und mit sauberer Kobaltnitratlösung geschüttelt, die das Thallium wieder extrahiert. Etwa 90% der Thallium-Aktivität werden wiedergewonnen.

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ANNOTATION

High frequency titration methods in the investigation of complex formation

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HARA and West[1] were the first to use high frequency titration (HFT) for the investigation of complex formation when they studied the reaction of EDTA with the lanthanides and certain rare metals. Pungor and Zapp[2] repeated this work and extended it to other reactions; they considered that the method had its limitations, particularly if the change in conductivity was very small near the end-point of the titration. We have found that the HFT method gives valuable information about the processes of complex formation in solutions, if the titration is carried out under conditions that give the steepest characteristic curve with the equipment used. Under these conditions break points are obtained on the titration curve at certain molar ratios of metal and complexing agent, and correspond to sharp changes in the electrical conductivity of the solution as a result of such reactions as displacement of metal ions from their EDTA complexes by addition of protons. This application of HFT must be supplemented by a parallel study based on preparative work and physico-chemical methods such as potentiometry, chromatography, optical activity, *etc.*

EXPERIMENTAL

Two variations of HFT are used in the investigation of complexes in solution. In the first, solutions of complexing agent and a salt of the metal are mixed in various molar ratios and the hydrogen ions released in the complex-formation are titrated with sodium hydroxide; the composition of the most stable complex is found from the number of protons released per metal ion. In the other method a solution of a salt of the metal is titrated with a solution of the complexing agent. and the breaks in the curve give the compositions of all the complexes formed. In our investigations we have used high frequency equipment types BY–IA and BY–2A;[3,4] automatic recording of the HFT curves is particularly useful. A very important function of HFT is for rapid assessment of the chelating properties of newly synthesised complexing agents.

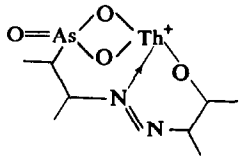
RESULTS AND DISCUSSION

Thorium complexes

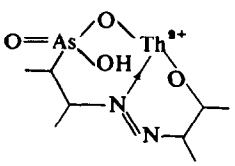
The reaction of thorium nitrate with a series of complexones has been investigated by HFT methods supplemented by preparative and potentiometric studies.[5] Except for the reaction with EDTA, thorium forms stable 1:1 complexes with 4-, 5- and 6-membered rings (at pH 9) with these reagents. With nitrilotriacetic acid (NTA) and uramildiacetic acid, thorium forms 1:2 complexes at pH 8. The reaction of thorium with a series of complexones containing from one to five carboxyl groups—hexamethylenediaminetetra-acetic acid (HMDTA), ethylenediamineoxyphenylacetic acid, oxyphenylethylenediaminediacetic acid, oxyethylethylenediaminetriacetic acid, and diethyl triaminepenta-acetic acid—has been investigated.[6] The reaction with HMDTA was studied to investigate the effect of steric factors (increase in polymethylene chain length and distance between iminodiacetic acid groups) on the stability of thorium complexes with complexones. Direct titration of thorium nitrate with HMDTA showed that a 1:1 complex was formed, and titration with sodium hydroxide showed that two protons were released per thorium ion, indicating the reaction $H_2X^{2-} + Th^{4+} \rightleftharpoons ThX + 2H^+$. The product is insoluble and is precipitated.[7] HFT has also been used to clarify the structure of the complex carbonates of thorium.[8] It had earlier been found that the most characteristic type of these compounds was the hydrated form, *e.g.*, $M_6Th(CO_3)_5 \cdot H_2O$, where M is a univalent ion. In such compounds the carbonate groups are bound to the thorium through the oxygen atom, but the number of carbonate groups bound to the central atom was uncertain. This problem was especially interesting in connection with the ammonium carbonate complex, which is characterised by its instability. HFT curves for potassium, sodium and ammonium carbonate solutions with thorium nitrate show two breaks. The first corresponds to the formation of the soluble carbonato complex

with a molar ratio of 1:4 for $Th:CO_3^{2-}$, and the second corresponds to precipitation of thorium carbonate when $Th:CO_3^{2-}$ is 1:2. The complex anion is therefore assigned the structure $Th(CO_3)_4^{4-}$ with coordination number 8 for the thorium.

Spectroscopic studies show that in arsenazo III complexes only one of the functional groups is involved in complex-formation, the other being left free as a result of a reduction of its reactivity by an inductive effect when the first group has formed a chemical bond with a cation.[9,10] In dilute acid solution (~0·1*M* hydrochloric acid), when thorium is present in excess the arsenazo III (R) complex is ThR, and at higher acidities (>1*M*) ThR_2 is formed with arsenazo III in excess. The spectrophotometric titration curves, however, do not give unambiguous evidence for these complexes, but the HFT curves for 10^{-3}–$10^{-4}M$ thorium nitrate and arsenazo III (titrated in both directions) show clearly that these formulae are correct. The formulae (I) and (II) shown for the ThR and ThR_2 are confirmed[9] by HFT determination of the number of protons released in formation of the complexes—3 for ThR and 4 for ThR_2. The proton of the sulphonic acid grouping is preferentially titrated first and takes no part in the complex formation.



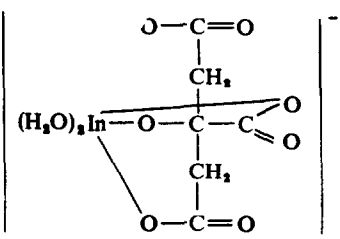
(I)



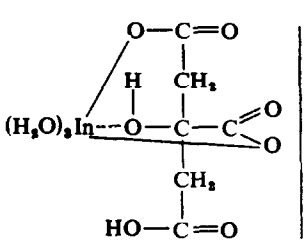
(II)

Indium complexes

By high frequency and potentiometric titration of various mixtures of indium(III) and citric acid by a solution of an alkali metal salt it has been shown that the indium citrate complex is a 1:1 complex.[12] When indium(III) chloride is titrated with sodium citrate, however, a binuclear complex In_2Cit is formed, which resembles those found for other metals with oxy-acids.[13–15] These results, taken in conjunction with those from ion-exchange and preparative work, show that when indium citrate complexes are formed both hydroxyl and carboxyl groups participate. If the coordination number of indium is taken as 6, then structures (III) and (IV) can be proposed for the 1:1 complex at pH 1–2 and pH 7·1 respectively.



(III)



(IV)

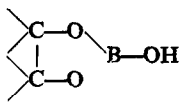
HFT studies have been made of the reaction of indium(III) with various complexones. With EDTA, DCTA (1,2-diaminocyclohexane-tetra-acetic acid) and HMDTA, indium forms 1:1 complexes.[16] From the stereochemistry of these complexes it would be expected that the stabilities would be in the order InDCTA > InEDTA > InHMDTA. The sharpness of the HFT peaks changes in just this order, and indicates that there is a definite relationship between the character of the peak on the HFT curve and the stability of the complex, but further study of this is required. HFT shows that indium forms two complexes with NTA—InNTA and $In(NTA)_2$.[16] Similar behaviour has been observed for indium and oxyethyliminodiacetic acid, and confirmed by potentiometric titration.

Plutonium complexes

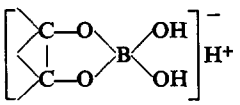
The reaction of plutonium(V) and EDTA has been studied[17] and the two breaks on the titration curve indicate the formation of the complexes PuEDTA and $Pu(EDTA)_2$. The results obtained have been combined with potentiometric data to yield (by Bjerrum's method) the stability constant for PuEDTA ($\log K = 12{\cdot}9 \pm 0{\cdot}1$).

Boron complexes

HFT has recently been used to investigate the reaction of hydroxystearinic acids (HSA) with boric acid in alcoholic solutions.[18] It was found that 1:1 complexes were formed with di-, tri- and tetrahydroxystearinic acids (m.p. 96°, 111° and 135° respectively) and a 1:2 complex (m.p. 160°) was also formed with tetrahydroxystearinic acid. Together with the results of low frequency conductivity measurements, these data confirm that a complex of the type (V) exists in solution. When the tetrahydroxystearinic borate complex was titrated (HFT) with sodium hydroxide in alcoholic solution, however, a complex of the type (VI) was found.



(V)



(VI)

These results indicate the HFT can be used to investigate the composition and structure of high molecular weight acids and polyalcohols in non-aqueous solvents or in mixed solvents.

Analytical applications

HFT can be used to locate the end-point in complexometric titrations, as for example in the titration of thorium with HMDTA. As HMDTA does not react with lanthanides at pH 4, it can be used for the determination of thorium in the presence of these elements (in ratios of La:Th up to 5) by the HFT method.[6]

At low enough pH (~1·5) NTA forms a stable complex with indium and does not react with zinc, cadmium, aluminium, nickel and cobalt. As shown in Table I, this allows indium to be determined in the presence of these elements. Similar results are obtained with DCTA.[19]

TABLE I.—HFT TITRATION OF INDIUM WITH NTA

Indium taken, *mg*	Other elements, *mg*					Indium found, *mg*	Error %
	Zn	Cd	Al	Ni	Co		
5·74						5·74	0
5·74	6·54	11·2	2·70	5·87	5·89	5·74	0
11·5	6·54	11·2	2·70	5·87	5·89	11·4	1
11·5	13·1	22·4	5·4	11·7	11·8	11·4	1

Complexometric high frequency titration is also used to determine yttrium oxide in mixtures of it with dysprosium or other lanthanide oxides. The average error is 5% relative, partly because an indirect method is used. A known weight of the oxide mixture is dissolved and titrated (HFT) with EDTA. The yttrium oxide content (X%) is then calculated from the formula

$$X = \frac{M_1(M_2A - 2a)}{2(M_2 - M_1)a} \times 100$$

where M_1 and M_2 are the formula weights of Y_2O_3 and the other lanthanide sesquioxide respectively, a is the weight of oxide mixture (in mg), and A is the number of mmoles of EDTA required to titrate the metals in that weight of oxide.

Inert electrolytes lower the accuracy of interpretation of the HFT curves,[20] but in spite of this limitation the technique is a promising one for the investigation of complex formation in solution and for the development of analytical methods, especially if its advantages and the possibility of automating it are taken into account.

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Summary—High frequency titration is a valuable tool in the study of complex formation in solutions, and the breaks in the titration curves can be used, in conjunction with the results of other physical methods, to determine the composition of the complexes formed. High frequency titration and other methods have been used to study the complexes formed by thorium, indium, plutonium(V) and boron with various complexing agents, and to develop methods for the determination of thorium and yttrium in rare earth mixtures, and of indium in the presence of zinc, cadmium, aluminium, nickel and cobalt.

Zusammenfassung—Die Hochfrequenztitration ist wertvoll bei der Untersuchung der Komplexbildung in Lösungen und die Stufen in den Titrationskurven können zusammen mit den Ergebnissen anderer physikalischer Methoden zur Ermittlung der Zusammensetzung der gebildeten Komplexe dienen. Die Hochfrequenztitration und andere Methoden wurden zur Untersuchung der Komplexe aus Thorium, Indium, Plutonium(V) und Bor mit verschiedenen Komplexbildnern verwendet und damit Vorschriften zur Bestimmung von Thorium und Yttrium in Gemischen seltener Erden und von Indium neben Zink, Cadmium, Aluminium, Nickel und Kobalt entwickelt.

Résumé—Le titrage en haute fréquence est un outil de grand intérêt dans l'étude de la formation de complexes en solutions, et l'on peut utiliser les brisures des courbes de dosage, conjointement aux résultats d'autres méthodes physiques, pour déterminer la composition des complexes formés. On a utilisé le titrage en haute fréquence et d'autres méthodes pour étudier les complexes formés par le thorium, l'indium, le plutonium (V) et le bore avec divers agents complexants, et pour développer des méthodes de dosage du thorium et de l'yttrium dans des mélanges de terres rares, et de l'indium en présence de zinc, cadmium, aluminium, nickel et cobalt.

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PRELIMINARY COMMUNICATIONS

Application of the drop method to the study of nucleation of sparingly soluble chelates

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PROGRESS in the study of nucleation from solution was slow until the advent of the drop method. This ingenious and elegant technique was devised by Vonnegut[1] to eliminate the effect of heterogeneous catalysts, *e.g.*, dust particles, glass walls, *etc.*, on nucleation processes. If a liquid is subdivided into discrete droplets of small enough volume, the heterogeneous matter present in the original volume of liquid will presumably be confined to a small fraction of the droplets. Nucleation of material in these droplets will occur as a heterogeneous process, whereas nucleation in the rest of the droplets will be governed only by the molecular characteristics of the pure material. The drop method has apparently only been used in conjunction with supercooling methods for obtaining supersaturated solutions, and has been applied in this manner with success to the study of the self-nucleation of a variety of compounds; polymers,[2,3] water,[4] tin[5] and n-alkanes.[6] Only limited success, however, has been achieved in the nucleation of salts from aqueous solution, *e.g.*, potassium nitrate[7] and ammonium iodide.[8] Supercooling is not generally a satisfactory method of producing supersaturated aqueous solutions of sparingly soluble species, however, because of the low solubility and the small working range of supercooling attainable. In fact, Melia[9] has stated that, "A new method of producing supersaturation in droplets (other than supercooling which sets a lower temperature limit of 0° and hence a supercooling limit of about 100°) would represent a major technical advance, . . . ".

This paper describes a new application of precipitation from homogeneous solution (PFHS) as a method of generating supersaturated solutions of sparingly soluble chelates, which may be combined effectively with drop techniques. In this combined technique, a PFHS reaction is started and some of the reaction medium is immediately emulsified into small droplets suspended in a suitable oil. The emulsion is then transferred to a microscope stage cell and observed either visually or photographically to study nucleation and growth processes as a function of time. To obtain critical supersaturations, kinetic rates, *etc.*, it is necessary to know the rate of production of nucleating material in the generation process. The kinetics of PFHS processes of nickel dimethylglyoxime and other chelates have been studied in great detail by Gordon *et al.*[10,11] and this work is being utilised in the analysis of nucleation experiments. Some of the experimental details of the combined technique and a description of a typical drop experiment are given below.

EXPERIMENTAL

The dispersion medium

An oil dispersion medium was needed that would not dissolve the reactants or products and that would be suitable for the preparation of reasonably stable, non-opaque, water-in-oil emulsions. Many oils were examined, *e.g.*, silicones, fluorocarbons, *etc.* The oils that seemed most suitable were Nujol (Saybolt viscosity 360–390 at 100°F, s.g. 0·880–0·900 at 60°F) and light mineral oil (Fisher Scientific Co., Saybolt viscosity 125–135).

Emulsification methods

An emulsification process was required that would produce monodisperse drops in a short time without introducing large temperature changes. Several methods were examined, *e.g.*, ultrasonic dispersion, syringe, aerosol spraying and mechanical mixing (various devices). The best results were obtained with a biological microhomogeniser.

Observation system

The system used was a Bausch and Lomb "Dynazoom" microscope fitted with polariser and analyser. A suitable cell for holding the emulsion in the light path was made by fixing a Teflon washer

on a microscope slide. Photographic techniques (still and cine) were used to obtain a large number of photographs of a large number of drops over long periods of time.

The effect of polarised light on nickel dimethylglyoximate

The use of crossed polarisers in the microscope led to some interesting observations on the properties of nickel dimethylglyoximate. A normal PFHS of nickel dimethylglyoximate was carried out with biacetyl monoxime as starting material. About 2 ml of this solution were placed in a Littman microscope cell on the stage. The solution was viewed under dark field conditions. The first crystals were blue and as the crystals grew larger they became red in the middle and remained blue at either end. Rotation of the sample caused extinction of these colours to occur at 90° intervals. These colours are polarisation colours and were determined by the quartz wedge technique to be second order blue and red. A birefringence-polarisation colour table was used (assuming approximate values for the birefringence of nickel dimethylglyoximate) to show that the red parts of the crystal were about twice the thickness of the blue parts.

A typical drop experiment

A PFHS reaction to generate nickel dimethylglyoximate was started by adding 10 ml of a solution $1{\cdot}25 \times 10^{-3}M$ in nickel and $1 \times 10^{-1}M$ in hydroxylamine hydrochloride (pH 7·1) to 10 ml of $2{\cdot}5 \times 10^{-2}M$ biacetyl monoxime. A small amount, 0·5 ml, of this mixture was quickly transferred to a microhomogeniser vessel which had been filled with Nujol. The whole mixture was emulsified by stirring at 14,000 rpm for 20 sec. The water-in-oil emulsion was quickly poured into a 50-ml measuring cylinder and allowed to stand. The cylinder was used as a very rough fractionating column in order to achieve removal of the larger drops. Part of the emulsion (2–3 drops) from near the top of the cylinder was transferred to the slide cell on the microscope stage.

About 100–200 drops were brought into the field (magnification 100–200 ×) and observed for 3–4 hr. After 18 min blue crystals were observed in a few of the drops and after 35 min many drops contained crystals. Drops which sank to the bottom of the cell and spread out on the glass (even in the presence of oil) produced crystals immediately. Photographs were taken at various times to complete a record of the number of drops containing crystals. The normal "beaker" reaction produced a nickel dimethylglyoximate precipitate in 3–4 min; the addition of oil had no effect on this reaction.

DISCUSSION

The results from the preliminary experiments indicate that PFHS techniques may be combined effectively with drop methods. The supersaturations of nickel dimethylglyoximate obtained were large (of the order of 10^3 or 10^4 times the equilibrium solubility) compared with those previously obtained in non-drop studies.[11] A much more detailed study of the system is now being carried out. The technique will be extended to a study of the nucleation of a series of metal aliphatic dioximates to obtain correlations between nucleation data and the structural characteristics of dioximates.

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Summary—The methods of producing supersaturated solutions of sparingly soluble chelates by precipitation from homogeneous solution have been combined with drop nucleation studies.

Zusammenfassung—Die Methoden, bei denen übersättigte Lösungen schwerlöslicher Chelate durch Fällung aus homogener Lösung erzeugt werden, wurden mit Untersuchungen der Tropfenkeimbildung kombiniert.

Résumé—On a combiné les méthodes de production de solutions sursaturées de chélates faiblement solubles par précipitation à partir de solutions homogènes avec les études d'amorçage par projection.

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Precipitation from homogeneous solution applied to the drop technique for the study of nucleation

(*Received* 15 *September* 1966. *Accepted* 23 *September* 1966).

MELIA, in his review on crystal nucleation from aqueous solution, pointed out the advantages of the droplet technique, first proposed by Vonnegut,[1] in the study of the nucleation process.[2] He also stated that methods of producing supersaturation within the droplets other than by supercooling, if devised, would be a "major technical advance", and that techniques need to be developed which would permit the observation of the number of secondary nuclei produced from a parent nucleus. The techniques of precipitation from homogeneous solution (PFHS) and high-speed motion picture photomicrography coupled with the droplet technique could possibly be used to produce the necessary supersaturation and to observe nucleation and crystal growth. Preliminary studies on the dispersion of water droplets in various oils and the application of PFHS to the droplet technique were therefore initiated. Some results of these preliminary studies are reported in this communication.

EXPERIMENTAL

Apparatus

A model MPS Lumex polarizing microscope (Fisher Scientific) was used throughout this investigation. The aqueous solutions were dispersed in the various oils by means of an osterizer (John Oster Manufacturing Company, Racine, Wisconsin) modified so that the total volume of the air-tight mixing chamber was about 125 ml.

Reagents

Except for the oils, all chemicals were of reagent grade quality.

Procedure

About 10 ml of a freshly-prepared PFHS reaction mixture (the conditions of which were adjusted so that a turbidity was observed about 7 min after mixing) were placed in the osterizer and enough mineral oil added so that all air was excluded from the system when the cap was in place. The osterizer was immediately turned on and allowed to operate for about 30 sec (5000 rpm). Two drops of the resulting oil-water mixture were removed from the osterizer and placed on a "hanging-drop" slide. The slide was then mounted on the stage of the polarizing microscope. With a magnification of 100–400 × and crossed polarizers, approximately 100 droplets were observed during an experiment.

RESULTS AND DISCUSSION

Initial experiments employing various lubricating, silicone and mineral oils indicated that a mixture of equal parts of air-free light and heavy mineral oils provided the best medium for dispersing the PFHS reaction mixtures. In this mixture most of the droplets remained dispersed for the 2–3 hr observation period.

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RESULTS AND DISCUSSION

Initial experiments employing various lubricating, silicone and mineral oils indicated that a mixture of equal parts of air-free light and heavy mineral oils provided the best medium for dispersing the PFHS reaction mixtures. In this mixture most of the droplets remained dispersed for the 2–3 hr observation period.

The following PFHS reactions have been successfully coupled with the droplet technique: nickel(II)—salicylaldehyde—hydroxylamine, nickel(II)—cyclohexanedione—hydroxylamine, nickel-(II)—cycloheptanedione—hydroxylamine, palladium(II)—cyclohexanedione—hydroxylamine, and palladium(II)—cycloheptanedione—hydroxylamine. In the case of the nickel(II)—salicylaldehyde—hydroxylamine system, supersaturations of about 1000 times the equilibrium solubility were attained before nucleation was observed.

It is apparent from these preliminary experiments that PFHS reactions can be coupled with the droplet technique for study of the nucleation process. Presently, a more detailed study of these systems is being carried out and a high-speed motion picture camera is being adapted for microscopic work.

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O. E. Hileman, Jr.

Summary—The technique of precipitation from homogeneous solution has been successfully coupled with the drop technique for study of the nucleation process.

Résumé—On a associé avec succès la technique de précipitation en solution homogène avec la technique de projection pour l'étude du processus d'amorçage.

Zusammenfassung—Das Verfahren der Fällung aus homogener Lösung wurde erfolgreich mit der Tropfenmethode zur Untersuchung des Keimbildungsprozesses kombiniert.

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LETTER TO THE EDITOR

Remarks on hexamminecobalt(III) carbonatoberyllate

SIR,

Monk and Exelby[1] have corroborated the conclusion reached by us[2] that the precipitate formed by the action of hexamminecobalt(III) chloride on a solution of the carbonato complex of beryllium has the composition proposed by Sen Gupta[3] and not that put forward by Pirtea.[4]

On the other hand they consider that this precipitate cannot be used for precise quantitative determination of beryllium, on the grounds that it consists of a mixture of the deca- and dodeca-hydrates described by Sen Gupta, the ratio of the two depending on the history of the precipitate. They state that if not too high an accuracy is required, the compound is suitable as a weighing form if it is kept for a long period at a relative humidity of 32–80%. For precise determination, they prefer to take advantage of the 2:1 mole ratio of beryllium to cobalt and determine the cobalt as a means of evaluating the amount of beryllium in the precipitate.

Monk and Exelby also state that "to prevent possible dehydration of the precipitate, the precipitate was not washed with absolute ethanol", but present no evidence that such an effect would occur. We consider that it would not, since in our experience, gathered over many years, washing with absolute (or 96%) ethanol or anhydrous acetone removes only the mother liquor, and the subsequent washing with ether and drying under suction from a water-pump removes only the wash-liquids. We are quite sure that no water of crystallisation is lost in the process, no matter how much ethanol is used or how long the precipitate is kept under reduced pressure.

We consider that keeping the precipitate at a relative humidity of 32–80% until it has reached constant weight is likely to be a protracted business, and moreover is unreliable as the wash-liquid used (60% aqueous ethanol) is not removed by this treatment, which may account for these authors having found more than 10 molecules of water of crystallisation in the formula. They are also mistaken in supposing that we and Pirtea used a desiccant (which they further presumed was "slow in action"). The precipitate was kept in an empty desiccator under a moderate vacuum. Although Pirtea suggested 15 min as the duration of the drying, we have found that longer periods make no difference, and that repetition of the process does not alter the weight of the precipitate (within the limits of accuracy of the weighing).

If the precipitate is washed with alcohol and ether and then kept under a moderate vacuum, it can be used as a good weighing form for beryllium. It contains 10 molecules of water per unit formula, and the conversion factor to beryllium is 0·0395. We have not found the dodecahydrate described by Sen Gupta.

Monk and Exelby's method of determining the beryllium through the cobalt content of the precipitate is fully justified in theory. It has been proposed[5] that the precipitate can be dissolved and the cobalt(III) reduced in alkaline solution. The cobalt(II) is then titrated with EDTA with Murexide as indicator. We have tried this method, but used Xylenol Orange as indicator and titrated at pH 4·5–5·0. The results were completely satisfactory, but somewhat less accurate than the gravimetric results; we think this is because of the increased number of operations needed and hence the number of sources of error. We would, however, recommend this method for the determination of small amounts of beryllium (<1 mg) and for routine macro determinations. An advantage is that the precipitate can be washed with a dilute ammonium carbonate solution and the washing with alcohol and ether is unnecessary.

We consider that the complexometric method proposed by Monk and Exelby[6] gives very accurate results, and would be very suitable for referee work, though it is perhaps rather more complicated than one would wish for routine analysis.

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Dom N2, Kv 97
Moscow D-98, U.S.S.R.
19 *January* 1966

A. V. VINAGRADOV

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GEGENSTROMIONOPHORESE—II*

EXPERIMENTELLE UNTERSUCHUNGEN

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(*Eingegangen am* 14 *April* 1966. *Angenommen am* 18 *Juli* 1966)

Zusammenfassung—Durch Anwendung neuer Apparaturen gelingt es, Prinzip und Verlauf der Gegenstromionophorese unter Verwendung anionischer Modellsubstanzen zu bestätigen. In Übereinstimmung mit der Theorie richten sich die Anionen von der Anode zur Kathode hin nach fallender Beweglichkeit aus. Zur Ausbildung des stationären Zustandes müssen bei der Anionentrennung Gegenstrom- und Anodenelektrolyt Anionen größerer, Ablauf- und Kathodenlösung Anionen kleinerer Beweglichkeit als das Trenngemisch enthalten. Feldstärkemessungen in einer Kammer mit kapillarem Trennspalt beweisen, daß die Feldstärke im stationären Zustand nicht gleichmäßig abfällt, sondern daß an den Grenzen benachbarter Zonen unterschiedlicher Ionenbeweglichkeiten sprunghafte Änderungen auftreten. Die Ausbildung dieses Feldstärkeprofils ist für die erhaltenen scharfen Trennungen verantwortlich. Durch Vergleich gemessener Feldstärkequotienten mit berechneten Beweglichkeitsquotienten wird die Berechnung unbekannter Ionenbeweglichkeiten möglich. Die sich in den Zonen einstellenden Konzentrationen werden durch die Beweglichkeiten der beteiligten Ionen und die Konzentration der Gegenstromlösung bestimmt.

IN der vorangehenden Mitteilung[1] wurden auf Grund theoretischer Betrachtungen allgemeine Bedingungen abgeleitet, die bei der Gegenstromionophorese zur Einstellung stationärer Verhältnisse führen und die automatische Steuerung des Trennvorganges ermöglichen.

Die vorliegende Arbeit dient der experimentellen Prüfung. Durch Trennungen von Modellsubstanzen, Messung des Feldstärkeverlaufs im Trennsystem und Bestimmung der Konzentrationsverhältnisse in eigens dazu entwickelten Apparaturen werden die wesentlichen Annahmen über den Verlauf von Gegenstromtrennungen experimentell bestätigt. Darüberhinaus wird die Trennung chemisch sehr ähnlicher Gemischtligandkomplexionen mit dem neuen Verfahren durchgeführt.

APPARATUREN FÜR DIE GEGENSTROMIONOPHORESE

Für die qualitative Beobachtung von Modelltrennungen und zur orientierenden Bestimmung der Einflüsse verschiedener Versuchsparameter dient eine einfache Gegenstromapparatur mit einer Trennkapillare.

Zur quantitativen Messung der Feldstärke- und Konzentrationsverhältnisse während des Trennvorgangs wird eine Meßkammer beschrieben, die den Zugang von außen zum Trennsystem gestattet.

Das Trennrohr

Beim Bau des Gegenstromtrennrohrs sind folgende Gesichtspunkte zu berücksichtigen:
(a) Verwendbarkeit von Kapillaren verschiedener Länge und verschiedenen Durchmessers.

* Mitteilung I: *Talanta* 1966, **13**, 1649.

(b) Genaue Regulierbarkeit der Gegenstromgeschwindigkeit.
(c) Bequeme Zuführung des Trenngemisches.
(d) Intensive Kühlung.
(e) Einfache Reinigung und Spülung.

Das Trennrohr Abb. 1 besteht aus einer Trennkapillare (1), an deren Enden zwei Aufweitungen (6 und 7) von 6 cm Länge und 1 cm Durchmesser angeschmolzen sind. Beide tragen Glasaufsätze (0,5 cm Durchmesser und 3 cm Länge), die mit den Elektrodentrögen (5 cm Höhe und 5 cm Durchmesser) verbunden sind. In den Glasaufsätzen befinden sich Steinwollediaphragmen. Durch das

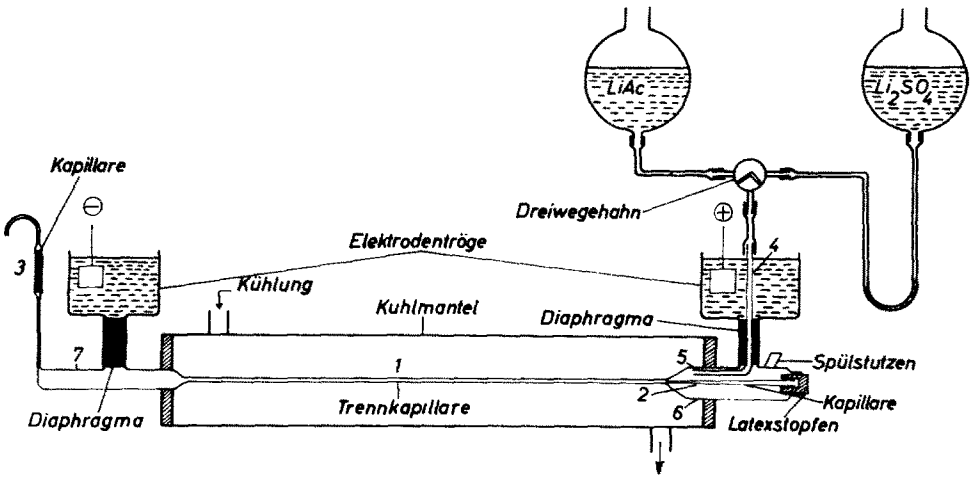

ABB. 1.—Schematischer Längsschnitt des Trennrohrs.

Anodendiaphragma führt eine Glasröhre (4) mit aufgesetztem Polyäthylenschlauch (5) in das aufgeweitete Glasrohr (6) bis kurz vor den Ansatz der Trennkapillare. Sie dient der Zufuhr der Elektrolytlösung (Lithiumacetat und-sulfat) die aus zwei Niveaugefäßen über einen Dreiwegehahn getrennt in das Trennrohr gelangen.

Die Aufweitung (7) unter der Kathode mündet in einem Kapillaraufsatz (0,1 cm Durchmesser) über den ein Polyäthylenschlauch mit einer feinen Kapillare (3) zur Regulierung der Gegenstromgeschwindigkeit gestülpt ist.

Die Zuführung des Trenngemisches erfolgt über eine weitere Kapillare (2) von ungefähr 6 cm Länge, die etwa 0,2 cm in die Trennkapillare hineinreicht. Gehalten wird sie von einem zur Hälfte angebohrten Latexstopfen, der gleichzeitig die Öffnung des Trennrohres abschließt. Somit gelangt das Trenngemisch unmittelbar in die Trennkapillare, wodurch Vermischung weitgehend ausgeschlossen wird.

Zur Abführung der Jouleschen Wärme einerseits und zur Aufrechterhaltung konstanter Temperaturverhältnisse in der Trennkapillare andererseits ist diese von einem Kühlmantel umgeben, durch den ein Glycerin-Wassergemisch von 0° aus einem Kryomaten gepumpt wird.

Die Anordung der zu trennenden Ionen nach steigender Beweglichkeit bereits vor Versuchsbeginn bewirkt eine Verkürzung der Trenndauer. Bei der Anionentrennung füllt man deshalb das Trennrohr zunächst blasenfrei mit Lithiumacetat-lösung. Mit Hilfe einer Injektionsspritze wird dann eine gewählte Menge der Trennlösung durch den Latexstopfen und die Zuflußkapillare (2) in die Trennkapillare (1) gedrückt. Anschließend spült man den Raum unterhalb der Anode durch Öffnen des Spülstutzens gut mit der Gegenstromlösung (Lithiumsulfat) aus.

Die Regulierkapillare (3) wird durch Ausziehen eines dickwandigen Glasrohres hergestellt. Ihre Auslaufgeschwindigkeit muß so groß sein, daß bei einer Niveaudifferenz zwischen der Gegenstromlösung und dem Ausfluß von etwa 40 bis 60 cm die Strömungsgeschwindigkeit in der Trennkapillare gerade die elektrolytische Wanderung der Ionen kompensiert. Durch Heben oder Senken des Niveaugefäßes kann die Gegenstromgeschwindigkeit reproduzierbar und in weiten Grenzen variiert werden.

Zur Vermeidung von Ionenverarmung, wählt man die Lösungen, in den Elektrodentrögen grundsätzlich konzentrierter als in der Trennkapillare, insbesondere, wenn von einer Elektrodenspülung während der Trennung abgesehen wird. Als Anodenlösung dient im allgemeinen 0,025–0,05 m Lithiumhydroxid, als Kathodenlösung ein Puffergemisch, das je 0,05 m an Lithiumacetat und Essigsäure ist.

Um die Apparatur von eventuell gebildeten Zersetzungs- und Hydrolyseprodukten bequem reinigen zu können, besteht sie aus mehreren Einzelteilen, die von Polyäthylenschläuchen zusammengehalten werden. Diese Aufgliederung hat den Vorteil, daß man die Trennkapillaren schnell auswechseln kann. Besonders haben sich Kapillaren von 20 cm Länge und 0,08 cm Durchmesser bewährt. Bei der meistens angelegten Gleichspannung von 3000 V entspricht das einer mittleren Feldstärke von 150 V/cm.

Meßkammer

Die Meßkammer ist grundsätzlich dem Trennrohr entsprechend aufgebaut, Abb. 2.

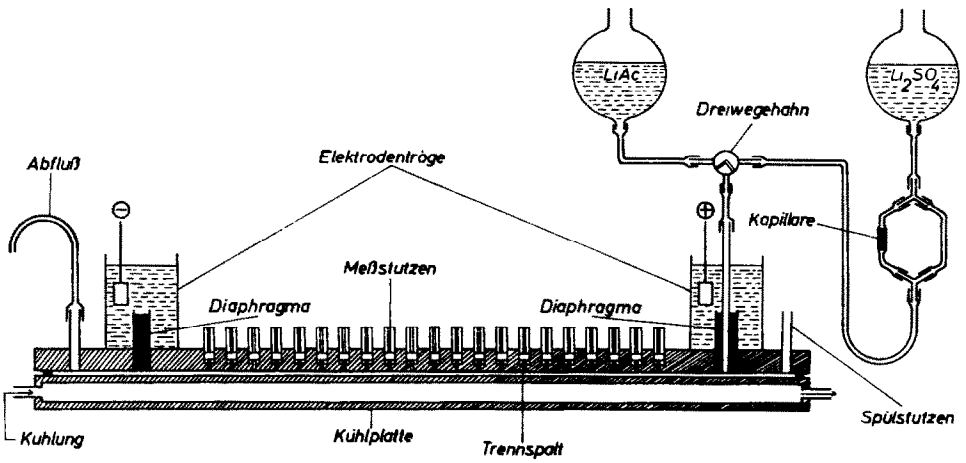

ABB. 2.—Schematischer Längsschnitt der Meßkammer.

Zwischen zwei 30 cm langen und 10 cm breiten Glasplatten werden zwei weiche Gummistreifen parallel zu einander ausgelegt, so daß sie einen Trennspalt bilden. Die obere Platte ist so beschaffen, daß sie während der Trennung mit Eis gekühlt werden kann; die untere ist an ein Kühlsystem angeschlossen (Glycerin-Wasser-Gemisch von 0°). Beide Platten werden von drei Kunststoffklammern zusammengehalten.

Im Abstand von 2 bzw. 3 cm von den Plattenenden entfernt, sind auf die obere Platte zwei Elektrodentröge geklebt, die über Bohrungen mit dem Trennspalt in Verbindung stehen. In diese Bohrungen werden PVC-Hülsen mit Steinwolldiaphragmen eingelassen.

Vier Glasröhren durch die Anodendiaphragmen führend, besorgen die Elektrolytzufuhr. Zwischen Plattenende und Anodentrog befinden sich zwei 0,4 cm Bohrungen mit PVC-Hülsen. Sie dienen als Spülstutzen. Hinter dem Kathodentrog bilden weitere sechs PVC-Hülsen in 0,35 cm Bohrungen den Auslauf der Kammer. Auslauf- und Spülbohrungen einschließend, grenzen zwei weitere Gummistreifen, senkrecht zu den beiden ersten angeordnet, den Trennspalt ab.

Die Gegenstromgeschwindigkeit wird mit einer Kapillare (Dosierkapillare) gesteuert, die in einer Schlauchverzweigung der Zuführung des Gegenstromelektrolyten befestigt ist.

Konzentrations- und Feldstärkemessungen erlauben 21 Meßstutzen, die im Abstand von je 1 cm zwischen den Elektrodentrögen liegen. Sie werden im folgenden näher beschrieben.

An eine Bohrung von 0,75 cm Höhe und 0,35 cm Durchmesser schließt sich eine engere Bohrung von 0,15 cm Durchmesser und 0,25 cm Höhe an, so daß die engere Bohrung im Trennspalt endet. Auf diese Art entsteht ein Absatz in der gesamten Bohrung. Darauf liegt ein 0,1 cm hohes PVC-Führungsplättchen mit einer 0,1 cm Bohrung. Eine 0,3 cm dicke Latexscheibe wird von einer fest an der oberen Bohrung anliegenden PVC-Hülse gegen das Führungsplättchen gedrückt. PVC-Hülse und Führungsplättchen haben die Aufgabe, eine Nadelelektrode, die durch die Latexscheibe gestochen wird, stets an der gleichen Stelle in den Trennspalt einzuführen, so daß bei Feldstärkemessungen der Abstand zwischen den einzelnen Meßstutzen als annähernd konstant angesehen werden kann. Die Latexscheibe verhindert den Zugang der Elektrolytlösungen an die Oberfläche der Glasplatte.

Wie im Trennrohr werden auch hier die Anionen bereits vor der eigentlichen Trennung nach steigender Beweglichkeit im Trennspalt angeordnet. Die Trennlösung wird mit einer Injektionsspritze durch einen der Meßstutzen direkt in den Trennspalt gedrückt.

Vor Anlegen der Spannung wird der direkte Weg des Gegenstromzulaufs geschlossen, so daß die

Regulierung der Gegenstromgeschwindigkeit über die Dosierkapillare und das Niveaugefäß mit der Gegenstromlösung erfolgen kann.

Der Anodentrog enthält im allgemeinen 0,5 m Lithiumhydroxid der Kathodentrog 0,5 m Lithiumacetat-Pufferlösung.

Die Trenndauer ist auf Grund der niedrigeren Feldstärken (*ca.* 80 V/cm) entsprechend höher als im Trennrohr.

Im Gegensatz zum Trennrohr kann man in dieser Apparatur den Verlauf der Trennung bis zur Einstellung stationärer Verhältnisse durch Feldstärkenmessungen verfolgen. Ebenso ist es möglich, dem Trennspalt durch die Meßstutzen Proben zu entmehmen, die der Klärung der Konzentrationsverhältnisse nach beendeter Trennung dienen.

Die Verwendung einer Abdeckplatte mit einer größeren Zahl im Abstand von 0,3 cm festeingelassener dünner Platindrähte zur Feldstärkemessung hat sich nicht bewährt, weil durch Polarisationselektrolyse gebildete kleine Gasbläschen im Trennspalt zu erheblichen Störungen Anlaß geben.

QUALITATIVE UNTERSUCHUNGEN AM TRENNROHR

Die auf Grund theoretischer Überlegungen gewonnenen Vorstellungen über den Ablauf und die Steuerung von Gegenstromtrennungen werden unter Verwendung von Modellsubstanzen experimentell geprüft. Für die visuelle, qualitative Beobachtung des Entmischungsvorgangs im Trennrohr und die Ausbildung des stationären Zustandes mit scharf abgegrenzten Zonen eignen sich besonders gefärbte Ionen mit großen Beweglichkeitsunterschieden, wie z.B. gelbe $[IrCl_6]^{2-}$-, blaue $[IrBr_6]^{2-}$-, violette MnO_4^--Ionen u.a.. Weiterhin werden durch Variation apparativer Parameter die günstigsten Bedingungen für eine hohe Trennschärfe bestimmt.

Zeitlicher Verlauf einer Trennung

Ein Gemisch mit $[IrCl_6]^{2-}$-und $[IrBr_6]^{2-}$-Ionen wird in der Trennkapillare zwischen Lösungen aus Lithiumacetat nahe der Kathode und Lithiumsulfat nahe der Anode angeordnet, Abb. 3*a*.

Bereits 3 Minuten nach Einschalten des Gegenstroms (Lithiumsulfatlösung) und der Hochspannung (3000 V) beginnt sich eine Front des Trenngemisches gegen die Ac^--Ionen auszubilden. Nach etwa 7 Minuten (Abb. 3*d*) besteht zwischen den blauen $[IrBr_6]^{2-}$-Ionen und dem Acetatbereich eine scharfe Grenze. Nach 9 Minuten ist die Trennung der gelben $[IrCl_6]^{2-}$-Ionen und der SO_4^{2-} -Ionen soweit fortgeschritten, daß sich zwischen beiden Ionenarten eine Grenze abzuzeichnen beginnt, die nach 12 Minuten ausgeprägt ist. Gleichzeitig schreitet die Trennung der Komplexionen fort, und die Entmischung ist nach *ca.* 15 Minuten beendet.

Die mit Abb. 3*g* wiedergegebene stationäre Anordnung der Zonen bleibt bei konstanten Versuchsbedingungen beliebig lange erhalten. Wird der Versuch unterbrochen, so vermischen sich die scharfen Grenzen durch Diffusion und Konvektion sehr schnell. Es genügt jedoch eine Trenndauer von wenigen Minuten, um die stationären Verhältnisse wiederherzustellen.

Änderungen der angelegten Spannung um 10% und mehr bzw. der Gegenstromgeschwindigkeit durch Heben oder Senken des Niveaugefäßes mit der Gegenstromlösung (Abb. 1) führen zu einer langsamen gleichmäßigen Verschiebung der Zonen um eine bestimmte Strecke in Richtung Anode oder Kathode bis wieder stationäre Verhältnisse erreicht sind. Bei solchen Wanderungen der Grenzschichten leidet die Trennschärfe nicht. Diese Beobachtungen bestätigen somit die Ausführungen über die Steuerung von Gegenstromtrennungen (I. Mitteilung, Abb. 2).

Einfluß der Konzentration des Gegenstromelektrolyten

Entsprechend der allgemeinen Arbeitstechnik wird ein Gemisch aus $[IrCl_6]^{2-}$- und $[IrBr_6]^{2-}$-Ionen, eingegrenzt zwischen Ac^-- und SO_4^{2-}-Ionen, getrennt. Die Gegenstromgeschwindigkeit wird so eingestellt, daß sich beide Komplexzonen nach Erreichen stationärer Verhältnisse etwa in Rohrmitte befinden, Abb. 4*a*.

Die Konzentration des Gegenstromelektrolyten wird schrittweise von zunächst 0,01 m (Abb. 4*a*) über 0,0075 m (Abb. 4*b*) und 0,005 m (Abb. 4*c*) auf 0,0025 m (Abb. 4*d*) erniedrigt.

Dazu wird nach gleichzeitiger Unterbrechung des elektrischen Stroms und des Gegenstroms die Gegenstromlösung im Niveaugefäß (Abb. 1) gegen die verdünntere ausgetauscht und der Raum vor der Trennkapillare unterhalb der Anode bei geöffnetem Spülstutzen quantitativ mit der neuen Lösung gefüllt. Die Lösung in der Trennkapillare wird von diesem Spülvorgang nicht betroffen. Bereits kurze Zeit nach Fortsetzung des Versuches erscheinen die Komplexzonen wieder scharf und zunächst in der ursprünglichen Länge. Sobald jedoch die verdünntere Lösung durch den Gegenstrom das

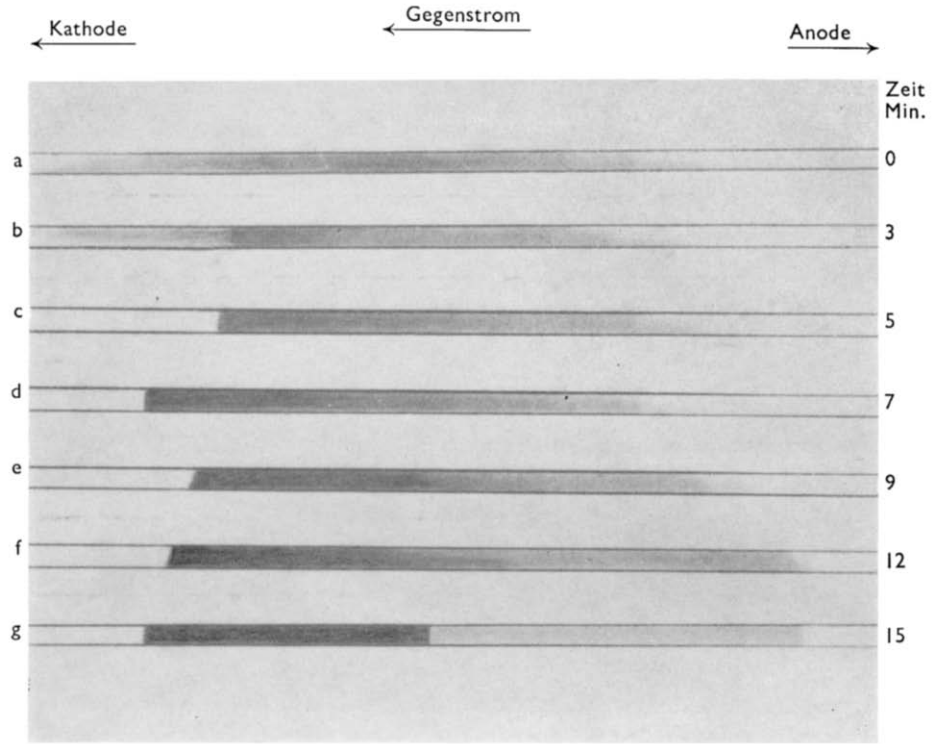

ABB. 3.—Zeitlicher Verlauf der Trennung von $[IrCl_6]^{2-}$ und $[IrBr_6]^{2-}$-Ionen.

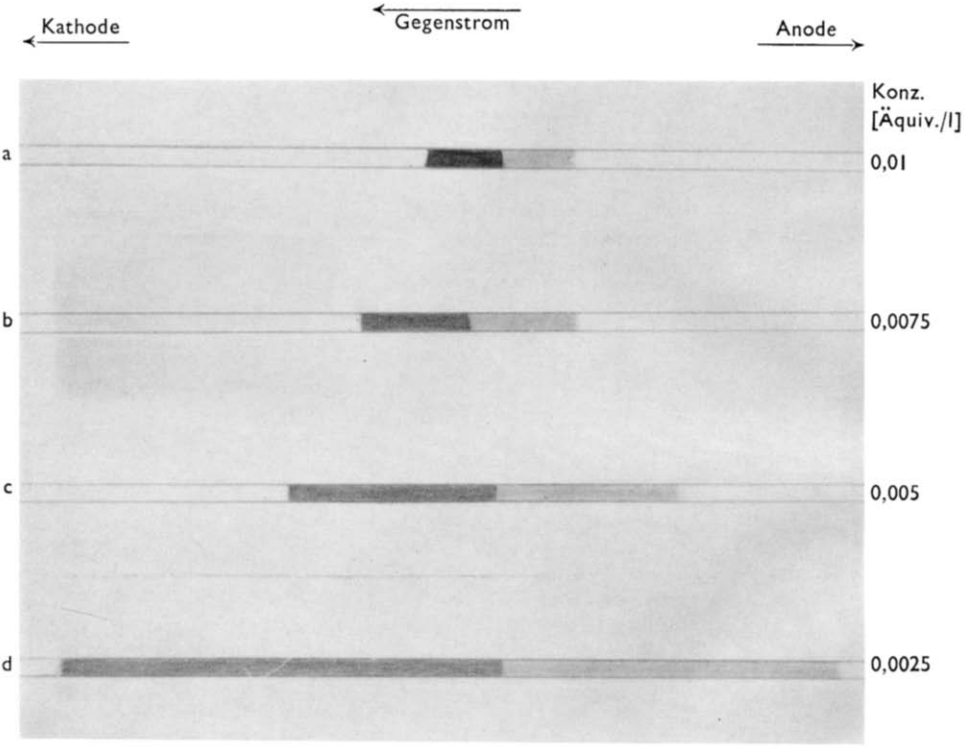

ABB. 4.—Konzentration des Trenngemisches in Abhängigkeit von der Konzentration des Gegenstromelektrolyten.

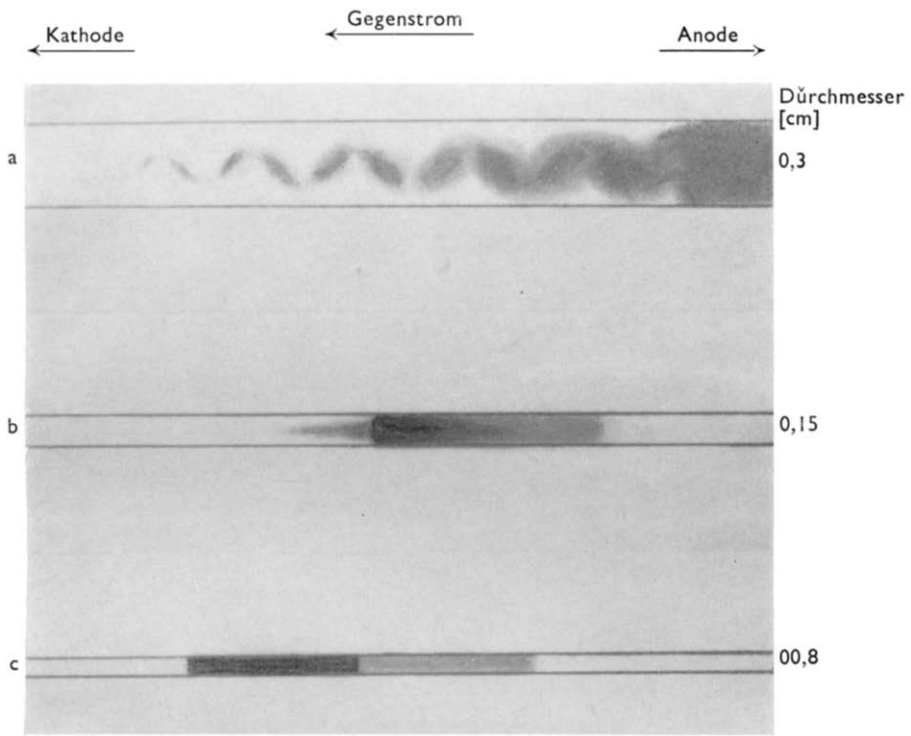

Abb. 5.—Abhängigkeit der Trennschärfe vom Kapillardurchmesser.

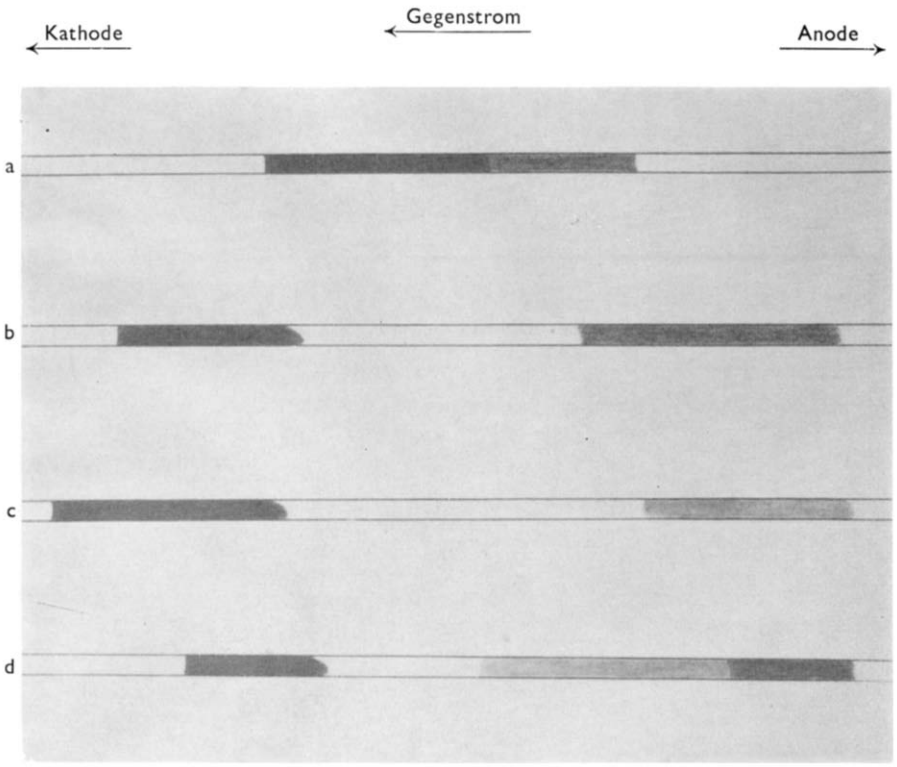

Abb. 6.—Mehrstofftrennungen.

Gebiet der Komplexzonen erreicht hat, dehnen sich die beiden Zonen um ein bestimmtes Stück aus und behalten dann wieder konstante Längen bei.

Die Abb. 4 zeigt anschaulich, daß durch die Änderung der Konzentration der Gegenstromlösung die Trennschärfe nicht beeinträchtigt wird, daß sich aber die Zonen im Trennrohr bei den einzelnen Verdünnungsschritten um die Hälfte, das Doppelte und Vierfache der ursprünglichen Länge ausdehnen.

Wie erwartet (I. Mitteilung, Gl. 16) besteht demnach eine direkte Proportionalität zwischen den Konzentrationen des Trenngemisches und des Gegenstromelektrolyten.

Abhängig keit der Trennschärfe vom Kapillardurchmesser

Um einheitliche Versuchsbedingungen zu gewährleisten und die vergleichende Beobachtung der Trennschärfen zu ermöglichen, werden drei Trennrohre verschiedenen Durchmessers zu einer Apparatur zusammengefaßt.

In einem Kühlmantel ausreichender Weite sind Kapillaren von 0,3; 0,15; 0,08 cm Durchmesser parallel zu einander eingesetzt. Die Stromzufuhr erfolgt über eine verzweigte Leitung von einem Hochspannungsgleichrichter aus. Wegen der höheren elektrischen Stromstärken bedingt durch die größeren Querschnitte der Kapillaren und der damit verbundenen Wärmeentwicklung, wird die übliche Spannung von 3000 V auf 2500 V erniedrigt.

Abb. 5 zeigt den stationären Zustand der Trennung eines $[IrBr_6]^{2-}/[IrCl_6]^{2-}$-Gemisches, wie er sich nach etwa einstündiger Trenndauer eingestellt hat.

Während in der engsten Kapillare bereits nach 15 Minuten eine exakte Trennung vorliegt (Abb. 5*c*), kommt es in der mittleren nur langsam zu einer Anreicherung der Komponenten (Abb. 5*b*). Einzelne Zonen sind nicht mehr zu erkennen. In der dicksten Kapillare wird der Hexabromokomplex mit dem Gegenstrom spiralförmig in den Acetatbereich hineingewirbelt (Abb. 5*a*).

Die Ursache für die schlechte Trennung in Kapillaren größeren Durchmessers ist in der bei allen ionophoretischen Trennungen auftretenden Konvektion zu suchen. Durch die gleichmäßig über den gesamten Querschnitt der Kapillare entstehende Joulesche Wärme baut sich von ihrer Mittelachse in Richtung zur gekühlten Außenwand ein Temperaturgradient auf. Die dadurch entstehenden Dichteunterschiede erzeugen bei der waagerechten Anordnung der Apparatur senkrecht zur Strömungsrichtung eine Thermokonvektion, die zur Ausbildung spiralförmiger Wirbel führt.

MEHRSTOFFTRENNUNGEN

Am Beispiel von Ionen, die sich in ihren Beweglichkeiten stärker unterscheiden, werden zunächst allgemeine Gesichtspunkte für Mehrstofftrennungen aufgezeigt.

Trennung von Ionen mit größeren Beweglichkeitsunterschieden

Durch die Trennung einer Anzahl Ionen wird qualitativ demonstriert, wie Trennschärfe, Trennzeit der einzelnen Ionen und die Gesamttrennzeit von Mehrkomponentengemischen zusammenhängen.

Abbildung 6 zeigt die stationären Zustände für die Trenngemische *a* bis *d*. In Tab. I sind die Ionen in ihrer Reihenfolge von der Kathode in Richtung Anode aufgeführt. Tabelle II enthält die Gesamttrennzeiten und die Trennzeiten für einzelne Ionenpaare. Aus Abb. 6 ergibt sich für die Beweglichkeiten der getrennten Ionen folgende qualitative Reihe:

$$Ac^- < [IrBr_6]^{2-} < BrO_3^- < [IrCl_6]^{2-} < MnO_4^- < SO_4^{2-}$$

Den Trennzeiten für die einzelnen Ionenpaare (Tab. II) ist zu entnehmen, daß die Differenz der Ionenbeweglichkeiten zwischen $[IrCl_6]^{2-}$ und BrO_3^- größer sein muß als z.B. zwischen $[IrBr_6]^{2-}$ und BrO_3^-. Der Vergleich der Trennschärfen ergibt, daß

diese um so exakter werden, je mehr sich die einzelnen Ionenpaare in ihren Beweglichkeiten unterscheiden, d.h. je kürzer die Trennzeiten sind.

Allgemein gilt für Mehrstofftrennungen die Regel, daß die Dauer der gesamten Trennung der Zeit entspricht, in der sich benachbarte Ionen mit der geringsten Beweglichkeitsdifferenz entmischen.

Wie Abb. 6 anschaulich zeigt, ist es vorteilhaft, farblose Ionen, in diesem Fall BrO_3^-, durch "Indikatorionen" zu markieren, indem man die farblose Zone durch kleine Gebiete gefärbter Ionen abgrenzt.

TABELLE I.—FOLGE DER IONEN IM STATIONÄREN ZUSTAND

Gemisch	Ionenfolge
a	$Ac^-/[IrBr_6]^{2-}/MnO_4^-/SO_4^{2-}$
b	$Ac^-/[IrBr_6]^{2-}/BrO_3^-/MnO_4^-/SO_4^{2-}$
c	$Ac^-/[IrBr_6]^{2-}/BrO_3^-/[IrCl_6]^{2-}/SO_4^{2-}$
d	$Ac^-/[IrBr_6]^{2-}/BrO_3^-/[IrCl_6]^{2-}/MnO_4^-/SO_4^{2-}$

TABELLE II.—TRENNZEITEN,

Gemisch	Gesamte Trennzeit *Min.*	Trennzeit für die Ionenpaare *Min.*			
		$[IrBr_6]^{2-}$ BrO_3^-	BrO_3^- MnO_4^-	BrO_3^- $[IrCl_6]^{2-}$	$[IrCl_6]^{2-}$ MnO_4^-
a	6				
b	45	45	10		
c	45	45		15	
d	45	45		15	30

Trennung von Ionen sehr ähnlicher Beweglichkeit

Während die bisher beschriebenen Trennungen im wesentlichen Modellfälle darstellen, ist die Trennung von Gemischtligandkomplexionen des Ir(IV), $[IrCl_xBr_{6-x}]^{2-}$ ($x = 0, 1, \ldots, 6$), ein Beispiel für die Trennung chemisch sehr ähnlicher Ionen.

Ein Lösungsgemisch mit allen Gliedern dieser homologen Komplexreihe wird zwischen Ac^-- und SO_4^{2-}-Ionen der Gegenstromtrennung unterworfen. Es stellt sich sehr schnell ein quasistationärer Zustand ein. Die Gemischtligandkomplexionen bilden zunächst eine gegen den Ac^-- und SO_4^{2-}-Bereich scharf abgegrenzte annähernd homogene Zone. Die Subfraktionierung, d.h. die Entmischung in sieben Zonen mit den einzelnen Gemischtligandkomplexionen vollzieht sich nur sehr langsam und führt nach etwa zwei Stunden zu dem endgültigen stationären Zustand.

Die Reihenfolge der Gemischtligandkomplexionen ist dieselbe wie bei der Hochspannungspapierionophorese. Die Beweglichkeitsabnahme erfolgt schrittweise bei Austausch von Chlorid gegen Bromid und dürfte für benachbarte Gemischtligandkomplexionen ungefähr 1,5 bis 2% betragen.

In Trennkapillaren von 0,08 cm Durchmesser und bei mittleren Feldstärken um 150 V/cm bilden sich zwischen den Zonen mit den einzelnen Gemischtligandkomplexionen noch scharfe Grenzen aus.

Es ist somit zu erwarten, daß auch Ionen noch größerer Ähnlichkeit wie z.B. Stereoisomere und gewisse Isotope nach diesem Prinzip mit der beschriebenen Versuchsanordnung bei ausreichend langer Versuchsdauer getrennt werden können.

UNTERSUCHUNGEN AN DER MESSKAMMER

Die Untersuchungen an der Meßkammer (Abb. 2) dienen der quantitativen experimentellen Prüfung der in der I-Mitteilung formulierten Zusammenhänge zwischen Ionenbeweglichkeit, Feldstärke- und Konzentrationsverlauf längs des Trennweges.

Feldstärkemessungen

Im Gegensatz zum Trennrohr kann man an der Meßkammer die Einstellung stationärer Verhältnisse messend verfolgen.

Im einfachsten Fall legt man Lithiumacetatlösung vor, der man mit der

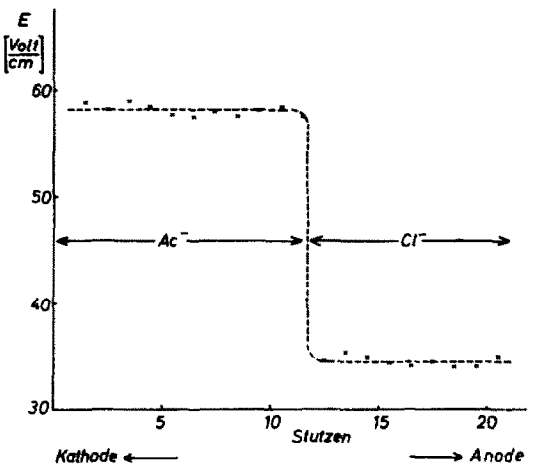

ABB. 7.—Feldstärkeverlauf für die Trennung Ac^-/Cl^-. Gegenstromlösung: 0,018 m LiCl; Spannung: 1200 V.

Gegenströmung z.B. Lithiumchloridlösung folgen läßt. Gemäß den allgemeinen Steuerbedingungen (1. Mitteilung, Abb. 2) kann man durch Variation der Gegenstromgeschwindigkeit, die entstehende Grenzschicht zwischen Ac^- und Cl^--Ionen an jeder Stelle der Meßkammer fixieren. Wegen der großen Beweglichkeitsunterschiede zwischen diesen Ionen stellt sich innerhalb weniger Minuten der stationäre Zustand ein.

Die Messung der Spannung zwischen jeweils benachbarten Stutzen an der Meßkammer (Abb. 2) mit einem möglichst stromlos messenden Voltmeter ergibt den Feldstärkeverlauf im Trennspalt. Er ist für die aneinander grenzenden Ac^-- und Cl^--Zonen in Abb. 7 graphisch dargestellt.

Die Feldstärke bleibt innerhalb einer Zone konstant und fällt an der Grenze zur nächsten scharf ab. Der Ersatz des Kations, z.B. Lithium gegen Kalium ist auf den Feldstärkeverlauf ohne Einfluß.

Bringt man entsprechend den Versuchen am Trennrohr ein Gemisch mit $[IrBr_6]^{2-}$- und $[IrCl_6]^{2-}$-Ionen zwischen Zonen mit Acetat und Sulfat, so stellt sich auch in der Meßkammer ein stationärer Zustand der Trennung ein. Das Ergebnis der Feldstärkemessung veranschaulicht Abb. 8.

Innerhalb der einzelnen Zonen ist die Feldstärke konstant, an den Grenzschichten

treten mehr oder weniger große Sprünge auf. Sie sind um so größer, je mehr sich die benachbarten Ionen in ihren Beweglichkeiten unterscheiden.

Die Meßstutzen verändern geringfügig den Querschnitt des Trennspaltes und beeinträchtigen dadurch etwas die scharfe Ausbildung der Fronten im stationären Zustand. Aus dem Feldstärkeverlauf der Abb. 8 ist ersichtlich, daß solche Störungen um so mehr in Erscheinung treten, je geringer die Feldstärkesprünge sind.

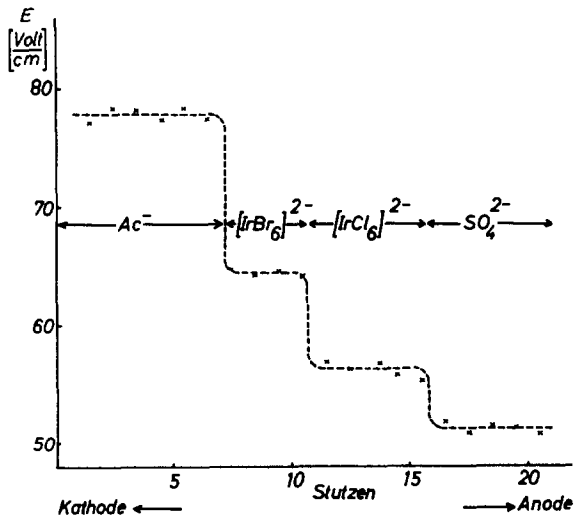

ABB. 8.—Feldstärkeverlauf für die Trennung $Ac^-/[IrBr_6]^{2-}/[IrCl_6]^{2-}/SO_4^{2-}$.

Obwohl die Meßkammer wegen apparativer Unzulänglichkeit für die Messung kleiner Feldstärkedifferenzen nicht geeignet ist, beweisen jedoch die Messungen bei Trennungen mit Ionen größerer Beweglichkeitsunterschiede die theoretischen Annahmen über den Feldstärkeverlauf, wie ein Vergleich der Abb. 8 mit Abb. 1 der 1. Mitteilung eindrucksvoll zeigt.

Störungen des normalen Feldstärkeprofils

Wichtigste Voraussetzung für die Messung reproduzierbarer Werte für die Feldstärke ist die Einstellung stationärer Verhältnisse. Diese sind mitunter nur scheinbar erreicht.

Die Trennkammer wird mit 0,01 m Lithiumsulfatgegenstromlösung bei 1600 V betrieben. Der Kathodenraum ist mit einer Lösung, die je 0,05 m an Lithiumacetat und Essigsäure ist, gefüllt. Im Anodentrog befindet sich 0,025 m Lithiumhydroxidlösung. Die Werte für die Feldstärken, wie sie nach einer Stunde (E_1) und nach fünf Stunden (E_2) gemessen werden, zeigt die Abb. 9.

Obwohl an der Apparatur keine Veränderungen vorgenommen wurden, weist Abb. 9 völlig verschiedene Feldstärkeverhältnisse für die beiden Messungen auf.

Die Erklärung liegt im Fehlen stationärer Verhältnisse. Da die Elektrodenlösungen nicht erneuert werden, hat sich ihre Zusammensetzung im Laufe des Experiments entscheidend verändert. Die Kathodenlösung ist nur noch schwach sauer.

Wesentlich für den Effekt sind jedoch die Vorgänge an der Anode. Aus der

ursprünglich alkalischen Anodenlösung wandern ständig Li^+-Ionen ab und SO_4^{2-}-Ionen zu. Außerdem entstehen anodisch H^+-Ionen, die am Anfang sofort durch die OH^--Ionen neutralisiert werden. In dem Maße, wie die Anodenlösung an Li^+-Ionen verarmt, nimmt ihre Konzentration an H^+-Ionen zu, bis sie schließlich sauer reagiert. Der Kationenstrom wird nach einer gewissen Zeit nicht mehr allein durch die Li^+-Ionen, sondern in erster Linie durch die schnelleren H^+-Ionen bewirkt. Im SO_4^{2-}-Bereich nimmt dementsprechend die Leitfähigkeit zu und die Feldstärke ab. Im

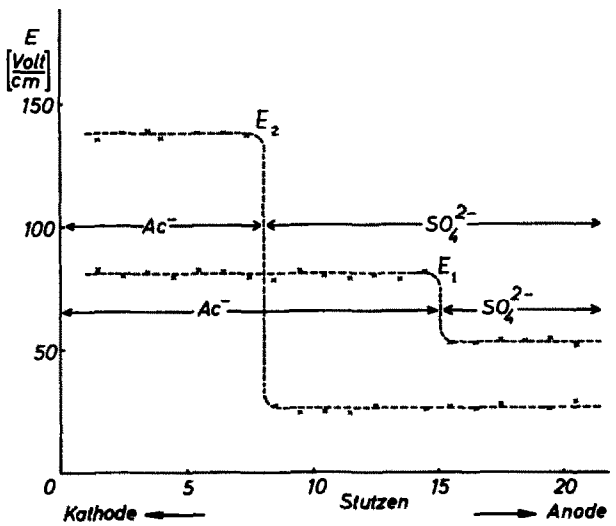

Abb. 9.—Anomaler Feldstärkeverlauf bei nichstationären Verhältnissen.

Ac^--Bereich treten dagegen die H^+-Ionen mit den Ac^--Ionen zu wenig dissoziierter Essigsäure zusammen. Es werden also Anionen weggefangen, die von der Kathode her nachwandern müssen, so daß sich eine Zone geringer Leitfähigkeit, d.h. hoher Feldstärke ausbildet.

Auch die kathodisch entstandenen und nicht neutralisierten OH^--Ionen stören. Bedingt durch ihre hohe Beweglichkeit wandern sie dem Gegenstrom entgegen und treffen auf die Komplexionen. Ir(IV)-Verbindungen werden jedoch im alkalischen Bereich leicht zu Ir(III)-Verbindungen reduziert, die leicht hydrolisieren.

Berechnung von Ionenbeweglichkeiten

Mit Hilfe der Beziehung

$$\frac{E_1}{E_2} = \frac{u_2}{u_1} \quad \text{(I. Mitteilung, Gl. 2)}$$

läßt sich eine unbekannte Ionenbeweglichkeit, z.B. u_2, aus einer bekannten, u_1, und dem Verhältnis der Feldstärken E_1/E_2, die sich im stationären Zustand in den Zonen zweier Ionenarten einstellen, berechnen.

Wie im vorangegangenen Kapitel beschrieben, ist für eine Anzahl Trennungen der Feldstärkeverlauf im Trennspalt gemessen worden. Erwartungsgemäß ergibt sich bei

Verwendung verdünnter Lösungen in allen Fällen unabhängig von der Feldstärke und der Art der Kationen im stationären Zustand für bestimmte Anionen stets das gleiche Feldstärkeverhältnis. Innerhalb der Meßgenauigkeit stimmen die Ergebnisse mit den Literaturwerten überein.

Aus den Feldstärkeverhältnissen, die sich zwischen Ac^-- bzw. SO_4^{2-}-Ionen einerseits und $[IrBr_6]^{2-}$- und $[IrCl_6]^{2-}$-Komplexionen andererseits bei etwa 0° und *ca.* 0,01 n Lösungen einstellen, ergeben sich für diese Temperatur und Konzentration für die beiden Komplexionen folgende Beweglichkeiten:

$$u_{[IrCl_6]^{2-}} = 3{,}01 \cdot 10^{-4}\ [cm^2 \cdot V^{-1} \cdot sec^{-1}]$$

$$u_{[IrBr_6]^{2-}} = 2{,}63 \cdot 10^{-4}\ [cm^2 \cdot V^{-1} \cdot sec^{-1}]$$

Außer durch apparative Unzulänglichkeiten der einfachen Meßkammer werden Fehler durch die unterschiedliche Feldstärke in den einzelnen Zonen verursacht. Im Gebiet hoher Feldstärke, z.B. im Ac^--Bereich, entsteht mehr Joulesche Wärme pro Volumeneinheit als z.B. in der SO_4^{2-}-Zone. Deshalb ist mit gewissen Temperaturunterschieden, die die Ionenbeweglichkeit beeinflussen, zwischen den Zonen zu rechnen. Weitere Schwierigkeiten bereitet die stromlose Messung hoher Potentialdifferenzen.

Konzentrationsbestimmungen

Die Konzentrationsbestimmungen an der Meßkammer (Abb. 2) werden parallel zu den Feldstärkemessungen vorgenommen. Sie dienen der Bestätigung, daß sich nach Erreichen stationärer Verhältnisse die Konzentrationen der einzelnen Zonen entsprechend der Kohlrauschbeziehung und der Gl. 16 der 1. Mitteilung verhalten.

Entsprechend der allgemeinen Arbeitsweise stellt man bei Vorlage von Ac^--Ionen und mit Cl^-- bzw. SO_4^{2-}-Ionen in der Gegenstromlösung stationäre Verhältnisse ein, so daß die zur Kathode hin liegende Hälfte des Trennspalts mit Ac^--Ionen, die andere mit den Anionen der größeren Beweglichkeit besetzt ist. Der Ablauf der Gegenstromlösung wird bei stationärem Betrieb stundenweise aufgefangen. Die qualitative Analyse ergibt, daß es sich dabei um verdünnte Acetatlösungen handelt, in denen keine Anionen aus dem Gegenstromzulauf nachzuweisen sind.

Die Probenahme aus dem Trennspalt der Meßkammer geschieht sofort nach Abschalten des Versuchs, indem mit einer Injektionsspritze, deren Nadel durch die Meßstutzen gestoßen wird, aus den beiden getrennten Zonen etwa je 0,5 ml Lösung angesaugt werden. Je nach der verwendeten Gegenstromlösung handelt es sich bei den Proben um verdünnte wäßrige Lösungen von Lithiumchlorid bzw. Kaliumchlorid in der ersten Zone und um Lithiumacetat bzw. Kaliumacetat in der zweiten Zone. Die Konzentrationsbestimmungen erfolgen gravimetrisch nach Umwandlung in die Sulfate, die zur Trockne eingedampft, bei schwacher Rotglut geglüht und anschließend auf einer Mikrowaage ausgewogen werden.

Die Analysen zeigen, daß die Konzentration von Gegenstromzulauf und erster Zone sowie Gegenstromablauf und letzter Zone nicht, wie berechnet,[1] übereinstimmen. Die Konzentration in der ersten Zone liegt bis 10% höher als die des Gegenstromzulaufs. Dafür dürften u.a. in erster Linie elektroosmotische Strömungen verantwortlich sein.

Die Konzentrationen der beiden Zonen (Cl) und (Ac) im Trennspalt verhalten sich jedoch entsprechend der Beziehung:

$$\frac{c_{(Cl)}}{c_{(Ac)}} = \frac{u_{M(Ac)} + u_{Ac}}{u_{M(Cl)} + u_{Cl}} \cdot \frac{u_{Cl}}{u_{Ac}} \quad \text{(I. Mitteilung, Gl. 16)}$$

Bei Verwendung von Lithiumsulfat-, Lithiumchlorid-, Kaliumsulfat- und Kaliumchlorid-gegenstromlösungen verschiedener Konzentrationen ergeben sich für die Konzentrationsverhältnisse zwischen den Zonen im Trennspalt stets die von der obigen Beziehung geforderten Werte. Wie erwartet, wird der Konzentrationssprung zwischen den Zonen beim Austausch von K^+- gegen Li^+-Ionen erheblich kleiner.

Die vorliegende Arbeit wurde im Institut für Analytische Chemie und Radiochemie der Universität des Saarlandes durchgeführt. Wir danken dem Direktor des Instituts, Herrn Prof. Dr. E. Blasius, für Unterstützung und Diskussion und der Deutschen Forschungsgemeinschaft, dem Bundesminister für Wissenschaftliche Forschung sowie der Wissenschaftlichen Gesellschaft der Universität des Saarlandes für die Bereitstellung von Mitteln und Apparaturen.

Summary—By use of a new apparatus it has been possible to confirm the principle and course of countercurrent ionophoresis, by applying it to model anionic substances. Qualitative investigation showed that the anions were arranged between the anode and cathode according to their mobilities. For the formation of a stationary state the anions in the anode and countercurrent electrolytes must have greater mobility, and the anions of the effluent and cathode electrolytes a lower mobility, than the anions in the mixture to be separated. Field intensity measurements in a chamber with a capillary separation gap show that there is a sharp change in the field intensity at the boundaries of the stationary zones, and this intensity profile is responsible for the sharp separations obtained. By comparison of field intensity factors and known mobilities it is possible to calculate other ionic mobilities. The concentrations of ions in the zones can be calculated from the ionic mobilities and the concentration of the countercurrent solution.

Résumé—Par l'emploi d'un nouvel appareil, on a pu confirmer le principe et le développement de l'ionophorèse à contre-courant, en l'appliquant à des substances anioniques modèles. Une recherche qualitative a montré que les anions se répartissaient entre l'anode et la cathode selon leurs mobilités. Pour la formation d'un état stationnaire, les anions des électrolytes d'anode et de contre-courant doivent avoir une mobilité plus grande, et les anions des électrolytes d'écoulement et de cathode, une mobilité plus faible que les anions dans le mélange à séparer. Des mesures d'intensité de champ dans un compartiment avec un intervalle de séparation capillaire montrent qu'il y a un changement marqué dans l'intensité de champ aux séparations des zones stationnaires, et ce profil d'intensité est responsable des séparations nettes obtenues. Par comparaison des facteurs d'intensité de champ et de mobilités connues, il est possible de calculer d'autres mobilités ioniques. On peut calculer les concentrations des ions dans les zones à partir des mobilités ioniques et de la concentration de la solution de contre-courant.

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CATION-EXCHANGE BEHAVIOUR OF SEVERAL ELEMENTS IN HYDROCHLORIC ACID—ORGANIC SOLVENT MEDIA

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Summary—In the present paper the cation-exchange characteristics of 20 elements towards the strongly acidic cation-exchange resin Dowex 50X8 in media containing varying concentrations of organic solvents and aqueous hydrochloric acid were investigated. Based on the determination of the distribution coefficients of these elements in the organic solvents methanol, ethanol, n-propanol, isopropanol, methyl glycol, acetone, tetrahydrofuran, and acetic acid, the conditions most suitable for their quantitative separation are indicated and discussed.

IN comparison to the relatively large number of comparable data available for the cation-exchange behaviour of the elements in pure aqueous hydrochloric acid solutions,[1,2] no attempt has so far been made to investigate systematically the broad field of mixed aqueous—organic solvent media containing hydrochloric acid.

The exchange behaviour of lithium, sodium and potassium,[3–11] and of magnesium, calcium, strontium and barium[7,9,12,13] in methanol—hydrochloric acid media has been investigated. Some of these systems were applied to the effective separation of lithium from other alkali metals, *e.g.*, by using 90% methanol—10% 12*M* hydrochloric acid as eluent for the lithium.[9] Under these conditions the distribution coefficients of lithium and sodium for example are 2 and 41 respectively. In media containing phenol as well as methanol and hydrochloric acid, lithium was separated from sodium and potassium.[14]

Cation-exchange separations of lithium, sodium and potassium[11,15] in ethanol—hydrochloric acid media have been reported and the adsorption of indium studied.[16]

In hydrochloric acid solutions containing isopropanol, uranium was separated from large quantities of bismuth.[17]

Relatively great attention has been paid to cation-exchange studies and separations of various elements with acetone—hydrochloric acid mixtures as eluents. They have been used to fractionate lithium, sodium and potassium;[5,18] to separate calcium from copper, zinc, mercury(II), cadmium, and iron(III);[19] copper from nickel;[20] iron, copper, zinc, and lead from cobalt and manganese; these metals from the alkali metals, alkaline earths, magnesium, molybdate, sulphate and phosphate;[21] and to separate bismuth, cadmium, indium, zinc, iron(III), copper(II), uranium(VI), cobalt, gallium and manganese(II).[22,23] Acetone—hydrochloric acid solutions as eluting agents have also been employed to separate copper and zinc.[24,25] The adsorption of cerium(III) and praseodymium(III) in acetone media was studied.[26] The behaviour of the latter rare earth element was also investigated in hydrochloric acid systems containing methanol, ethanol, isopropanol, methyl ethyl ketone and glycol.[27]

Similarly in the same solvent—hydrochloric acid mixtures the adsorption behaviour of scandium was studied,[28] and a method for the separation of copper from iron with ethyl methyl ketone—hydrochloric acid as eluent was reported.[20] An effective separation of large amounts of iron(III) from cobalt, nickel and aluminium is possible by using tetrahydrofuran—hydrochloric acid mixtures as eluents.[29]

From this literature survey it is seen that cation-exchange in hydrochloric acid—organic solvent media has received attention only with respect to the solution of specific separation problems or has been used to study the adsorption behaviour of several metal ions in only one solvent or of only one or a small group of elements in several different organic solvents. The correlation of the various adsorption data obtained in these media by the various authors is extremely difficult because cation-exchange resins of various types were used. For this reason and to obtain a more complete picture of the adsorption characteristics and separation possibilities of elements in organic solvent media, the research work presented in this paper was performed, using the most frequently employed cation-exchange resin Dowex 50 in mixtures of 8 organic solvents containing hydrochloric acid. For this purpose the effect of increasing concentration of organic solvent from 0 to 90% in solutions with a constant overall acidity of 0·6*M* hydrochloric acid, and the effect of acidity ranging from 0·15 to 1·2*M* overall acidity at the constant concentration of organic solvent of 90%, were investigated by measuring the distribution coefficients in these media. From the distribution coefficients thus obtained, the possibilities of separating the elements investigated from one another are indicated and discussed.

EXPERIMENTAL

Reagents

Ion-exchange resin. The air-dried strongly acidic cation-exchanger Dowex 50X8 (100–200 mesh, hydrogen form) was used for the batch experiments.

Standard solutions. Exactly weighed amounts of Mg, Ca, UO_2(II), Mn(II), Co, Ni, Cu(II), Zn, Cd, Pb, Fe(III), Al, Ga, In, Bi, Th, Zr, Ce(III), V(V) and Mo(VI) as chlorides were dissolved in 6*M* or 12*M* hydrochloric acid to give solutions containing 5 mg of the element/ml.

Solvents. The reagent-grade pure organic solvents used were: methanol, ethanol, n-propanol, isopropanol, methyl glycol, acetic acid, tetrahydrofuran and acetone.

Determination of the various elements

Most of the elements investigated (in amounts exceeding *ca.* 100 μg) were determined titrimetrically, by suitable chelatometric methods with EDTA (disodium salt) as the titrant. Uranium was determined fluorometrically[30] and microgram quantities of the other elements were determined spectrophotometrically.[31]

Determination of distribution coefficients

The weight distribution coefficient is defined by the equation:

$$K_d = \frac{\mu\text{g of element/g of resin}}{\mu\text{g of element/ml of solution}}.$$

The method employed for determining the distribution coefficients of the elements in the various mixtures was the batch equilibrium method (batch method). Each equilibrium experiment was performed with 20 ml of a mixture consisting of 0–90% of the organic solvent, 10% of hydrochloric acid, and water up to 100%, and containing 5 mg of the element in question. To this mixture 1 g of resin was added and the solution was agitated on a shaking machine for 12 hr, then the resin was filtered off and the element determined in the filtrate. The experimental error of the measurements of the distribution coefficients was usually ±5–10% for low K_d-values (below 100), but for high values an error of 10–20% was frequently observed.

RESULTS AND DISCUSSION

In Tables I—XVII the metal ions are arranged in the same order. The distribution coefficients of cerium and thorium were in all cases larger than 2×10^3 and were not determined exactly. In those cases in which results are not given, experimental difficulties were encountered (*e.g.*, in the case of lead and aluminium the solubility was often too small).

TABLE I.—DISTRIBUTION COEFFICIENTS IN AQUEOUS METHANOLIC 0·6*M* HYDROCHLORIC ACID

Ion	Methanol concentration, %					
	0	20	40	60	80	90
UO_2(II)	40	45	67	144	207	85
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zr(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	~2	~2	~2	~2	~2	~2
V(V)	5	5	6	~5	~4	~4
Fe(III)	84	96	89	57	34	6
Al(III)	186	300	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ga(III)	242	324	637	$>10^3$	242	2·4
In(III)	1	1	<1	<1	<1	<1
Bi(III)	<1	<1	<1	<1	<1	<1
Mg(II)	33	40	50	109	188	288
Ca(II)	74	106	192	447	$>10^3$	$>10^3$
Pb(II)	~1	9	12	18	35	50
Zn(II)	39	35	21	5	<1	<1
Cd(II)	6	6	5	4	2	2
Cu(II)	32	34	41	53	31	6·6
Mn(II)	80	100	140	180	190	200
Co(II)	44	50	65	161	197	209
Ni(II)	46	49	72	102	168	250

Aliphatic Alcohol Media

In Tables I–IV, IX–XII, the distribution coefficients measured in hydrochloric acid—aliphatic alcohol mixtures (methanol, ethanol, n-propanol and isopropanol) are shown.

Uranium(VI), thorium(IV), zirconium(IV) and cerium(III)

It is seen that in all cases the adsorption of uranium is less than that of thorium. With increasing concentration of the aliphatic alcohol the uranium adsorption decreases, while that of thorium remains virtually constant so that a separation of uranium from thorium is possible. Cerium and zirconium show a behaviour similar to thorium. Thus these elements can be separated from uranium but not from thorium. It is to be expected that other lanthanide ions will behave very similarly to cerium.

When the concentration of hydrochloric acid is increased, the adsorption of uranium decreases considerably while the adsorption of thorium, cerium and zirconium is only slightly affected by a change in the acidity of the hydrochloric acid—aliphatic alcohol mixtures. Therefore a ready separation of uranium from thorium, cerium and zirconium is possible at 0·6*M* or higher overall acidities of the mixtures.

TABLE II.—DISTRIBUTION COEFFICIENTS IN AQUEOUS ETHANOLIC 0·6*M* HYDROCHLORIC ACID

Ion	Ethanol concentration, %					
	0	20	40	60	80	90
UO_2(II)	40	46	70	137	180	315
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zr(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	~2	~2	~2	~2	~2	~2
V(V)	5	~5	~5	~5	~5	~5
Fe(III)	84	134	134	134	46	7
Al(III)	186	300	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ga(III)	242	358	535	$>10^3$	268	4
In(III)	1	1	<1	<1	<1	<1
Bi(III)	<1	<1	<1	<1	<1	<1
Mg(II)	33	46	74	159	327	535
Ca(II)	74	113	246	620	$>10^3$	$>10^3$
Pb(II)	~1	13	17	22	57	91
Zn(II)	39	35	17	3	<1	<1
Cd(II)	6	6	3	3	3	2
Cu(II)	32	38	58	91	81	24
Mn(II)	80	124	150	198	241	248
Co(II)	44	55	86	147	270	290
Ni(II)	46	55	92	191	311	366

TABLE III.—DISTRIBUTION COEFFICIENTS IN AQUEOUS n-PROPANOLIC 0·6*M* HYDROCHLORIC ACID

Ion	n-Propanol concentration, %					
	0	20	40	60	80	90
UO_2(II)	40	61	41	102	159	266
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zr(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	~2	~2	~2	~2	~2	~2
V(V)	5	~10	~30	~40	~10	~5
Fe(III)	84	100	100	81	54	<1
Al(III)	186	315	680	>10	$>10^3$	$>10^3$
Ga(III)	242	247	786	$>10^3$	769	11
In(III)	1	<1	<1	<1	<1	<1
Bi(III)	<1	<1	<1	<1	2·3	22·7
Mg(II)	33	37	66	143	390	522
Ca(II)	74	115	175	400	$>10^3$	$>10^3$
Pb(II)	~1	5·3	7	21	70	110
Zn(II)	39	26	25	5	<1	<1
Cd(II)	6	6	6	6	6	6
Cu(II)	32	52	52	63	72	22
Mn(II)	80	118	147	189	241	248
Co(II)	44	55	86	143	376	376
Ni(II)	46	55	92	153	520	10^3

TABLE IV.—DISTRIBUTION COEFFICIENTS IN AQUEOUS ISOPROPANOLIC 0·6*M* HYDROCHLORIC ACID

Ion	Isopropanol concentration, %					
	0	20	40	60	80	90
UO_2(II)	40	60	120	224	400	500
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zr(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	~2	~2	~2	~2	~2	~2
V(V)	5	~5	~5	~5	~5	~5
Fe(III)	84	166	166	166	166	166
Al(III)	186	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ga(III)	242	$>10^3$	$>10^3$	$>10^3$	3	<1
In(III)	1	<1	<1	>1	<1	<1
Bi(III)	<1	<1	<1	<1	<1	<1
Mg(II)	33	35	38	100	153	260
Ca(II)	74	68	75	182	405	$>10^3$
Pb(II)	~1	20	20	25	38	16
Zn(II)	39	38	37	38	36	33
Cd(II)	6	4	<1	<1	<1	<1
Cu(II)	32	40	42	44	46	53
Mn(II)	80	214	342	703	$>10^3$	$>10^3$
Co(II)	44	52	44	40	52	47
Ni(II)	46	55	55	55	62	76

TABLE V.—DISTRIBUTION COEFFICIENTS IN 0·6*M* HYDROCHLORIC ACID IN AQUEOUS METHYL GLYCOL SOLUTION

Ion	Methyl glycol concentration, %					
	0	20	40	60	80	90
UO_2(II)	40	45	51	56	61	2
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zr(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	~2	~2	~2	~2	~2	~2
V(V)	5	~5	~5	~5	~5	~5
Fe(III)	84	148	146	96	4	4
Al(III)	186	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ga(III)	242	323	$>10^3$	$>10^3$	7	7
In(III)	1	1	<1	<1	<1	<1
Bi(III)	<1	104	137	118	176	370
Mg(II)	33	47	78	151	254	292
Ca(II)	74	144	183	491	10^3	$>10^3$
Pb(II)	~1	25	23	10	<1	<1
Zn(II)	39	36	10	<1	<1	<1
Cd(II)	6	<1	<1	<1	<1	<1
Cu(II)	32	48	60	58	8	<1
Mn(II)	80	227	304	475	567	215
Co(II)	44	187	329	1,066	414	80
Ni(II)	46	51	107	196	208	138

Molybdenum(VI) and vanadium(V)

These show identical behaviour in methanol, ethanol and isopropanol, but in n-propanol—hydrochloric acid media a separation of molybdenum from vanadium should be possible because molybdenum is much less strongly adsorbed than vanadium.

Both molybdenum and vanadium are practically non-adsorbable from 90% alcoholic media, so no separation is possible in this way in any of the alcohols.

TABLE VI.—DISTRIBUTION COEFFICIENTS IN 0·6*M* HYDROCHLORIC ACID IN AQUEOUS ACETIC ACID

Ion	Acetic acid concentration, %					
	0	20	40	60	80	90
UO_2(II)	40	42	54	65	22	14
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zr(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	~2	~2	~2	~2	~2	~2
V(V)	5	~5	~5	~5	~5	~5
Fe(III)	84	89	78	36	2	1·5
Al(III)	186	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ga(III)	242	308	324	180	<1	<1
In(III)	1	<1	<1	<1	<1	<1
Bi(III)	<1	<1	23	31	2·3	3·5
Mg(II)	33	57	81	102	174	184
Ca(II)	74	118	202	236	$>10^3$	$>10^3$
Pb(II)	~1	9	8	38	96	367
Zn(II)	39	31	7	<1	<1	<1
Cd(II)	6	<1	<1	<1	<1	<1
Cu(II)	32	49	42	17	2·6	1·5
Mn(II)	80	216	115	105	71	23
Co(II)	44	63	63	96	100	120
Ni(II)	46	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$

Iron(III), aluminium(III), gallium(III), indium(III) and bismuth(III)

At all concentrations of aliphatic alcohols investigated indium is practically not retained by the resin except from 60% isopropanol, from which it is retained slightly. A similar behaviour is shown by bismuth although in some cases rather irregular variations of its K_d values occur.

In all hydrochloric acid—aliphatic alcohol mixtures gallium shows maximum adsorption at 60% of alcohol and then the distribution coefficient decreases considerably when the alcohol concentration is increased to 90%.

Aluminium is in all cases strongly adsorbed at practically all alcohol concentrations, with 80% alcohol mixtures a separation of aluminium from gallium and indium in all four aliphatic alcohols is possible.

In practically all media the K_d-value of iron(III) decreases with an increase in the concentration of the organic component of the mixtures.

An increase in the acid concentration does not change the adsorbability of aluminium appreciably. It is strongly adsorbed at all hydrochloric acid concentrations (at an overall acidity of 1·2*M* hydrochloric acid, the solubility of aluminium chloride is very small so that no measurements of the distribution coefficients were possible under these conditions).

Because indium is not adsorbed over the acidity range from 0·15 to 1·2*M* hydrochloric acid and the adsorption of iron(III) decreases very strongly with increasing acidity, a separation of iron or indium from aluminium can be performed in all four aliphatic alcohols.

Magnesium(II), calcium(II) and lead(II)

When the alcohol concentration is increased the adsorption of these ions shows only a slight increase. A simple separation of the first two is not possible because of the similarity of their distribution coefficients. Thus a fractionation of these metal ions would only be possible by means of elution chromatography.

TABLE VII.—DISTRIBUTION COEFFICIENTS IN 0·6*M* HYDROCHLORIC ACID IN AQUEOUS TETRAHYDROFURAN

Ion	Tetrahydrofuran concentration, %					
	0	20	40	60	80	90
UO_2(II)	40	77	76	77	11	<1
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zr(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	~2	~2	~2	~2	~2	~2
V(V)	5	~5	~5	~5	4	3
Fe(III)	84	166	134	17	~1	~1
Al(III)	186	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ga(III)	242	268	704	39	8	~1
In(III)	1	<1	<1	<1	<1	<1
Bi(III)	<1	<1	<1	<1	<1	<1
Mg(II)	33	38	60	109	159	179
Ca(II)	74	188	207	281	422	655
Pb(II)	~1	16	10	4	<1	<1
Zn(II)	39	24	10	<1	<1	<1
Cd(II)	6	<1	<1	<1	<1	<1
Cu(II)	32	34	41	29	<1	<1
Mn(II)	80	184	274	292	355	176
Co(II)	44	52	69	138	108	6
Ni(II)	46	52	95	172	227	113

With an increase in acidity, the K_d-values of calcium and magnesium which are greater than 2×10^3 decrease slightly. As in the case of the 0·6*M* hydrochloric acid—aliphatic alcohol mixtures a separation of these two elements from each other would also be rather difficult at lower or higher concentrations of this acid.

A similar adsorption behaviour is observed in the case of lead although its distribution coefficient is in all cases smaller than that of the alkaline earth ions.

Zinc(II) and cadmium(II)

The adsorption of zinc from methanol, ethanol and n-propanol decreases when the concentration of the organic component in the mixtures is increased. If the amount of alcohol is 80% or higher, zinc is not retained at all by the resin. From the isopropanol—hydrochloric acid mixtures zinc is adsorbed to the same extent at all alcohol concentrations.

In methanol, ethanol and isopropanol media the adsorption of cadmium decreases with an increase of the alcohol concentration while in n-propanol no change of the

distribution coefficient of cadmium by variation of the alcohol content of the mixtures is observed.

Separations of zinc from cadmium should be possible in all four hydrochloric acid—alcohol systems. The best separation can very probably be obtained when using as eluent a hydrochloric acid—isopropanol mixture containing a high percentage of this alcohol.

At higher hydrochloric acid concentrations both elements are only very weakly adsorbed so that separations in such mixtures are not readily possible.

TABLE VIII.—DISTRIBUTION COEFFICIENTS IN 0·6*M* HYDROCHLORIC ACID IN AQUEOUS ACETONE

Ion	Acetone concentration, %					
	0	20	40	60	80	90
UO_2(II)	40	54	96	102	4	<1
Th(IV)	>10³	>10³	>10³	>10³	>10³	>10³
Zr(IV)	>10³	>10³	>10³	>10³	>10³	>10³
Ce(III)	>10³	>10³	>10³	>10³	>10³	>10³
Mo(VI)	~2	~1	~1	~1	<1	<1
V(V)	~5	~3	~1	~1	~1	<1
Fe(III)	84	78	78	11	<1	<1
Al(III)	186	329	>10³	>10³	>10³	>10³
Ga(III)	242	280	10³	27	<1	<1
In(III)	1	<1	<1	<1	<1	<1
Bi(III)	<1	<1	<1	<1	<1	<1
Mg(II)	33	48	80	156	264	332
Ca(II)	74	105	234	605	>10³	>10³
Pb(II)	~1	15	7·4	<1	<1	<1
Zn(II)	39	31	4	<1	<1	<1
Cd(II)	6	3	2	~2	~2	~2
Cu(II)	32	41	64	56	<1	<1
Mn(II)	80	85	132	275	216	4
Co(II)	44	56	80	169	77	<1
Ni(II)	46	55	111	220	250	227

Copper(II) and manganese(II)

The adsorption of copper increases slightly as the concentration of aliphatic alcohol increases to 80%, whereafter it decreases. The adsorption of manganese increases in methanol, ethanol and isopropanol mixtures. A separation of copper from manganese is easily possible in hydrochloric acid—isopropanol mixtures.

When the concentration of hydrochloric acid increases the adsorption of copper decreases rapidly while that of manganese does not show pronounced variations.

A separation of copper from manganese is possible in media of higher hydrochloric acid concentrations containing methanol, n-propanol or isopropanol. From ethanol solutions both elements are retained by the resin to about the same extent so that no separations are possible.

Cobalt(II) and nickel(II)

In virtually all cases cobalt and nickel show the same adsorption behaviour and their K_d-values increase with increasing concentration of aliphatic alcohol. Because the K_d-value of iron(III) decreases when the concentration of the organic components of the mixtures is increased, a separation of cobalt and nickel from iron is possible in

TABLE IX.—DISTRIBUTION COEFFICIENTS IN 90% METHANOL MIXTURES CONTAINING 10% OF HYDROCHLORIC ACID OF VARIED MOLARITY

Ion	Final HCl concentration, *M*				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	>10³	880	85	9	<1
Th(IV)	>10³	>10³	>10³	>10³	>10³
Zr(IV)	>10³	>10³	>10³	>10³	>10³
Ce(III)	>10³	>10³	>10³	>10³	>10³
Mo(VI)	>2	>2	~2	~2	~2
V(V)	>5	>5	5	~5	~5
Fe(III)	>10³	123	6	<1	<1
Al(III)	—	>10³	>10³	>10³	>10³
Ga(III)	>100	>10	2·4	<1	<1
In(III)	~1	~1	<1	<1	<1
Bi(III)	<1	147	<1	193	<1
Mg(II)	>10³	843	288	78	66
Ca(II)	>10³	>10³	>10³	>10³	10³
Pb(II)	—	73	50	25	13
Zn(II)	22	<1	<1	<1	<1
Cd(II)	5	2	2	2	<1
Cu(II)	300	58	6·6	<1	<1
Mn(II)	>10³	703	200	44	25
Co(II)	>10³	561	209	52	29
Ni(II)	>10³	700	250	63	33

TABLE X.—DISTRIBUTION COEFFICIENTS IN 90% ETHANOL MIXTURES CONTAINING 10% OF HYDROCHLORIC ACID OF VARIED MOLARITY

Ion	Final HCl concentration, *M*				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	10⁴	>10³	315	70	10
Th(IV)	>10³	>10³	>10³	>10³	>10³
Zr(IV)	>10³	>10³	>10³	>10³	>10³
Ce(III)	>10³	>10³	>10³	>10³	>10³
Mo(VI)	>2	>2	~2	<2	<1
V(V)	>5	>5	~5	<5	<1
Fe(III)	>10³	152	7	<1	<1
Al(III)	—	>10³	>10³	>10³	>10³
Ga(III)	8	6	4	<1	<1
In(III)	<1	<1	<1	<1	<1
Bi(III)	<1	147	<1	176	<1
Mg(II)	>10³	>10³	535	356	210
Ca(II)	>10³	>10³	>10³	>10³	>10³
Pb(II)	—	135	91	63	49
Zn(II)	12	<1	<1	<1	<1
Cd(II)	3	2	2	2	<1
Cu(II)	337	105	24	4	2
Mn(II)	>10³	>10³	248	167	124
Co(II)	>10³	634	270	187	70
Ni(II)	>10³	411	366	227	100

TABLE XI.—DISTRIBUTION COEFFICIENTS IN 90% n-PROPANOL MIXTURES CONTAINING 10% OF HYDROCHLORIC ACID OF VARIED MOLARITY

Ion	Final HCl concentration, *M*				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	530	330	266	15	<1
Th(IV)	>10^3	>10^3	>10^3	>10^3	>10^3
Zr(IV)	>10^3	>10^3	>10^3	>10^3	>10^3
Ce(III)	>10^3	>10^3	>10^3	>10^3	>10^3
Mo(VI)	>2	2	~2	~1	<1
V(V)	>5	~5	~5	~3	<1
Fe(III)	>10^3	89	<1	<1	<1
Al(III)	—	>10^3	>10^3	>10^3	>10^3
Ga(III)	17	15	11	<10	>1
In(III)	<1	<1	<1	<1	<1
Bi(III)	<1	147	22	176	<1
Pb(II)	<1	147	22·7	17·6	<1
Mg(II)	>10^3	>10^3	522	462	340
Ca(II)	>10^3	>10^3	>10^3	>10^3	>10^3
Pb(II)	—	125	110	96	82
Zn(II)	<1	<1	<1	<1	<1
Cd(II)	6	6	6	2	<1
Cu(II)	518	118	22	<1	<1
Mn(II)	>10^3	>10^3	114	100	80
Co(II)	>10^3	601	376	147	19
Ni(II)	>10^3	>10^3	10^3	313	166

TABLE XII.—DISTRIBUTION COEFFICIENTS IN 90% ISOPROPANOL MIXTURES CONTAINING 10% OF HYDROCHLORIC ACID OF VARIED MOLARITY

Ion	Final HCl concentration, *M*				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	>10^3	>10^3	500	70	<1
Th(IV)	>10^3	>10^3	>10^3	>10^3	>10^3
Zr(IV)	>10^3	>10^3	>10^3	>10^3	>10^3
Ce(III)	>10^3	>10^3	>10^3	>10^3	>10^3
Mo(VI)	~2	~2	~2	~2	~2
V(V)	~5	~5	~5	~5	~5
Fe(III)	>10^3	170	166	~1	<1
Al(III)	—	>10^3	>10^3	>10^3	>10^3
Ga(III)	~1	<1	<1	<1	<1
In(III)	<1	<1	<1	<1	<1
Bi(III)	<1	<1	<1	<1	<1
Mg(II)	>10^3	>10^3	260	194	84
Ca(II)	>10^3	>10^3	>10^3	>10^3	>10^3
Pb(II)	—	191	116	90	80
Zn(II)	39	38	33	30	25
Cd(II)	<1	<1	<1	<1	<1
Cu(II)	300	128	53	5	<1
Mn(II)	>10^3	>10^3	>10^3	274	180
Co(II)	>10^3	851	47	20	12
Ni(II)	>10^3	>10^3	76	60	52

methanol, ethanol and n-propanol. From an isopropanol medium all three elements are adsorbed to about the same extent.

When the concentration of hydrochloric acid is increased cobalt and nickel are decreasingly adsorbed from all four alcohols. A separation of these two elements from iron is possible when the hydrochloric acid concentration is 0·6*M* or higher.

TABLE XIII.—DISTRIBUTION COEFFICIENTS IN 90% METHYL GLYCOL MIXTURES CONTAINING 10% OF HYDROCHLORIC ACID OF VARIED MOLARITY

Ion	Final HCl concentration, *M*				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	370	200	2	<1	<1
Th(IV)	>10³	>10³	>10³	>10³	>10³
Zr(IV)	>10³	>10³	>10³	>10³	>10³
Ce(III)	>10³	>10³	>10³	>10³	>10³
Mo(VI)	~2	~2	~2	~2	~2
V(V)	~5	~5	~5	~5	~5
Fe(III)	6	5	4	2·6	<1
Al(III)	>10³	>10³	>10³	>10³	>10³
Ga(III)	~10	~8	7	~1	<1
In(III)	<1	<1	<1	<1	<1
Bi(III)	<1	136	370	193	<1
Mg(II)	813	292	292	116	50
Ca(II)	>10³	>10³	>10³	>10³	>10³
Pb(II)	—	2	<1	<1	<1
Zn(II)	<1	<1	<1	<1	<1
Cd(II)	2	~1	<1	<1	<1
Cu(II)	44	5	<1	<1	<1
Mn(II)	703	365	215	12	3
Co(II)	>10³	>10³	414	16	3
Ni(II)	>10³	523	138	39	27

Methyl Glycol Media

The results of measurements of the distribution coefficients of the various elements in hydrochloric acid—methyl glycol media are shown in Tables V and XIII.

Uranium(VI), thorium(IV), zirconium(IV) and cerium(III)

The behaviour of these elements with increasing methyl glycol concentration is virtually the same as that observed in the hydrochloric acid—aliphatic alcohol mixtures. A fractionation of thorium, zirconium and cerium is not possible but these three elements can be separated as a group from uranium. While the adsorption behaviour of uranium in media containing up to 80% methyl glycol is very similar to that observed in the aliphatic alcohols a further increase in methyl glycol concentration decreases the K_d-value of uranium considerably. This is in accordance with observations made earlier with respect to its adsorption behaviour towards the strongly basic anion-exchange resin Dowex 1 on which it is exceptionally strongly adsorbed from a mixture consisting of 90% methyl glycol and 10% 6*M* hydrochloric acid,[32,33] *i.e.*, in such a medium it forms a very stable anionic chloro-complex and hence is not retained by Dowex 50.

Molybdenum(VI) and vanadium(V)

These two elements show an adsorption behaviour similar to that observed in methanol, ethanol and n-propanol media and a separation of molybdenum from vanadium is impossible.

Iron(III), aluminium(III), gallium(III), indium(III) and bismuth(III)

As in the aliphatic alcohol media the adsorption of iron(III) decreases considerably at high methyl glycol concentrations. Aluminium is strongly adsorbed at all concentrations of this organic solvent. The same applies to gallium up to concentrations of 60% methyl glycol, whereafter the adsorption decreases. Indium is not taken up by

TABLE XIV.—DISTRIBUTION COEFFICIENTS IN 90% ACETIC ACID MIXTURES CONTAINING 10% OF HYDROCHLORIC ACID OF VARIED MOLARITY

Ion	Final HCl concentration, *M*				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	140	40	14	<1	<1
Th(IV)	>10^3	>10^3	>10^3	>10^3	>10^3
Zr(IV)	>10^3	>10^3	>10^3	>10^3	>10^3
Ce(III)	>10^3	>10^3	>10^3	>10^3	>10^3
Mo(VI)	~2	~2	~2	~2	~2
V(V)	~5	~5	~5	~5	~5
Fe(III)	3	2	1·5	<1	<1
Al(III)	>10^3	>10^3	>10^3	>10^3	>10^3
Ga(III)	<1	<1	<1	<1	<1
In(III)	<1	<1	<1	<1	<1
Bi(III)	<1	147	~3	214	<1
Mg(II)	>10^3	548	184	135	68
Ca(II)	>10^3	>10^3	>10^3	>10^3	>10^3
Pb(II)	—	765	367	90	70
Zn(II)	<1	<1	<1	<1	<1
Cd(II)	<1	<1	<1	<1	<1
Cu(II)	4	3	1·4	<1	<1
Mn(II)	241	114	23	6	<1
Co(II)	>10^3	143	120	12	<1
Ni(II)	>10^3	>10^3	>10^3	25	20

the resin at any methyl glycol concentration. A methyl glycol concentration of 70% seems to be the best medium to effect a separation of aluminium, gallium and indium. In contrast to its behaviour in the aliphatic alcohols bismuth is rather strongly retained by the resin, especially at higher concentrations of methyl glycol.

Magnesium (II), calcium (II), lead (II), zinc (II), cadmium (II), copper (II) and manganese (II)

These elements show in hydrochloric acid—methyl glycol media a behaviour which is similar to that observed in the aliphatic alcohols. A separation of copper from manganese can be effected in 90% methyl glycol.

Cobalt (II) and nickel (II)

In methyl glycol—hydrochloric acid solutions cobalt and nickel show about the same behaviour as in methanol, ethanol and n-propanol media, and can be separated from iron(III). Their separation together with aluminium, bismuth, manganese, calcium and magnesium from iron can also be effected.

TABLE XV.—DISTRIBUTION COEFFICIENTS IN 90% TETRAHYDROFURAN MIXTURES CONTAINING 10% OF HYDROCHLORIC ACID OF VARIED MOLARITY

Ion	Final HCl concentration, *M*				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	42	<1	<1	<1	<1
Th(IV)	>10^3	>10^3	>10^3	>10^3	>10^3
Zr(IV)	>10^3	>10^3	>10^3	>10^3	>10^3
Ce(III)	>10^3	>10^3	>10^3	>10^3	>10^3
Mo(VI)	~2	~2	~2	~2	~2
V(V)	~3	~3	3	~3	~3
Fe(III)	~1	~1	~1	<1	<1
Al(III)	>10^3	>10^3	>10^3	>10^3	>10^3
Ga(III)	>1	>1	~1	<1	<1
In(III)	<1	<1	<1	<1	<1
Bi(III)	<1	<1	<1	<1	<1
Mg(II)	>10^3	522	179	57	41
Ca(II)	>10^3	>10^3	655	490	324
Pb(II)	—	<1	<1	<1	<1
Zn(II)	<1	<1	<1	<1	<1
Cd(II)	<1	<1	<1	<1	<1
Cu(II)	5	<1	<1	<1	<1
Mn(II)	700	189	176	10	<1
Co(II)	>10^3	>10^3	6	<1	<1
Ni(II)	>10^3	313	113	17	10

TABLE XVI.—DISTRIBUTION COEFFICIENTS IN 90% ACETONE MIXTURES CONTAINING 10% OF HYDROCHLORIC ACID OF VARIED MOLARITY

Ion	Final HCl concentration, *M*				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	<1	<1	<1	<1	<1
Th(IV)	>10^3	>10^3	>10^3	>10^3	>10^3
Zr(IV)	>10^3	>10^3	>10^3	>10^3	>10^3
Ce(III)	>10^3	>10^3	>10^3	>10^3	>10^3
Mo(VI)	~1	~1	<1	<1	<1
V(V)	~4	~1	<1	<1	<1
Fe(III)	<1	<1	<1	<1	<1
Al(III)	>10^3	>10^3	>10^3	>10^3	>10^3
Ga(III)	<1	<1	<1	<1	<1
In(III)	<1	<1	<1	<1	<1
Bi(III)	<1	<1	<1	<1	<1
Mg(II)	>10^3	>10^3	332	247	191
Ca(II)	>10^3	>10^3	>10^3	>10^3	>10^3
Pb(II)	—	<1	<1	<1	<1
Zn(II)	<1	<1	<1	<1	<1
Cd(II)	~2	~2	~2	~1	<1
Cu(II)	3	~1	<1	<1	<1
Mn(II)	700	96	4	<1	<1
Co(II)	500	17	<1	<1	<1
Ni(II)	>10^3	597	227	81	74

At lower hydrochloric acid concentrations the behaviour of cobalt and nickel is virtually the same as in the methanol media of comparable acidity. There exists however, the possibility of separating cobalt from nickel when the acidity is increased above 0·9*M* hydrochloric acid. Furthermore a separation of iron from cobalt can be effected.

Acetone and Tetrahydrofuran Media

In Tables VII, VIII, XV and XVI are shown the results of determinations of the distribution coefficients of the various metal ions in acetone and tetrahydrofuran media containing hydrochloric acid. The elements show a similar behaviour in both organic solvents.

TABLE XVII.—DISTRIBUTION COEFFICIENTS IN HYDROCHLORIC ACID OF VARIED MOLARITY

Ion	Final HCl concentration, *M*				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	326	113	40	<1	<1
Th(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zr(IV)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^2$	$>10^2$
Mo(VI)	~2	~2	~2	~2	~2
V(V)	~5	~5	5	2	2
Fe(III)	$>10^3$	$>10^3$	84	54	17
Al(III)	$>10^3$	500	186	100	50
Ga(III)	$>10^3$	700	242	150	100
In(III)	5	4	1	<1	<1
Bi(III)	~1	<1	<1	<1	<1
Mg(II)	683	355	33	12	7
Ca(II)	10^3	100	74	17	14
Pb(II)	~2	>1	~1	<1	<1
Zn(II)	177	76	39	17	6
Cd(II)	100	60	6	<1	<1
Cu(II)	180	140	32	19	<1
Mn(II)	500	190	80	13	10
Co(II)	715	188	44	24	12
Ni(II)	369	177	46	20	18

Uranium (VI), thorium (IV), zirconium (IV) and cerium (III)

Thorium, cerium and zirconium show the same behaviour as in the organic solvent media discussed before. The adsorption of uranium decreases with increasing concentration of the organic component. A separation of thorium, cerium and zirconium from uranium is possible at higher concentrations of acetone or tetrahydrofuran, while thorium, cerium and zirconium cannot be fractionated at any concentrations of these two solvents.

At higher hydrochloric acid concentrations uranium is practically not adsorbed whereas thorium, cerium and zirconium are still strongly retained and hence their separation from uranium is easily possible.

Other elements

Vanadium, molybdenum, aluminium, gallium, indium, calcium, magnesium, zinc, cadmium, lead, copper and manganese show a behaviour similar to that observed in the media discussed earlier.

With tetrahydrofuran as the organic component of the mixtures a good separation of copper from manganese is possible at a tetrahydrofuran concentration of 90%. A similar separation can be effected when the acetone concentration is 80%.

A complete separation of iron(III), cobalt and nickel is possible by using in succession 80% tetrahydrofuran—20% 3*M* hydrochloric acid and 90% tetrahydrofuran—10% 6*M* hydrochloric acid mixtures as eluents. From a column of Dowex 50 the first eluent removes the iron(III) and then cobalt is removed by the second eluent, leaving nickel on the resin.[29]

At lower hydrochloric acid concentrations separations of the following pairs of metal ions can also be carried out: in both solvents: aluminium—indium, aluminium—iron, cobalt—nickel and iron—nickel.

A separation of uranium from large amounts of bismuth can be effected by using a mixture of isopropanol and aqueous hydrochloric acid.[34]

Acetic Acid Media

The results of measurements of distribution coefficients of the elements in acetic acid media containing hydrochloric acid are shown in Tables VI and XIV. A comparison of these with those representing the systems discussed before shows that the behaviour of the elements in acetic acid is very similar to that in the other organic solvents so that no detailed discussion will be presented.

Water Media

In Table XVII the behaviour of the elements in pure aqueous solutions containing varying concentrations of hydrochloric acid is shown. In these systems fewer possibilities exist for the separation of the various metal ions from one another than in the media containing organic solvents. That this is generally true has been amply demonstrated[35] and can in several cases be explained theoretically by the CIESE-effect.[29,36,37]

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Résumé—On a étudié, dans le présent mémoire, les caractéristiques d'échange cationique de 20 éléments vis-à-vis de la résine cationique fortement acide Dowex 50X8 dans des milieux contenant des concentrations variables de solvants organiques et d'acide chlorhydrique aqueux. En se basant sur la détermination des coefficients de partage de ces éléments dans les solvants organiques méthanol, éthanol, n-propanol, isopropanol, méthylglycol, acétone, tétrahydrofuran et acide acétique, on indique les conditions les plus convenables pour leur séparation quantitative et en discute.

Zusammenfassung—In dieser Arbeit wurden die Kationenaustauscheigenschaften von 20 Elementen am stark sauren Kationenaustauscharz Dowex 50X8 untersucht in Medien, die organische Lösungsmittelen. und wäßrige Salzsäure in verschiedenen Konzentrationen enthielten. Auf Grund der Bestimmung der Verteilungskoeffizienten dieser Elemente in den organischen Lösungsmitteln Methanol, Äthanol, n-Propanol, Isopropanol, Methylglycol, Aceton, Tetrahydrofuran und Essigsäure werden die besten Bedingungen für ihre quantitative Trennung angegeben und diskutiert.

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SPECTROPHOTOMETRIC STUDY OF THE REACTION OF THE URANYL ION WITH 4-(2-THIAZOLYLAZO) RESORCINOL

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Summary—The uranyl ion forms only 1:1 chelates with 4-(2-thiazolylazo)resorcinol (TAR) in solution, $UO_2(TAR)H^+$ being formed below pH 3 and $UO_2(TAR)$ above pH 3·5. The latter complex may also be precipitated at pH > 3. The quantitative formation of $UO_2(TAR)$ at pH 7·5–7·8 in solutions containing a small excess of reagent and some triethanolamine as buffer can be used for the sensitive spectrophotometric determination of uranium. Several interfering ions can be masked with a mixture of sodium fluoride, cyclohexanediaminetetraacetic acid and 5-sulphosalicylic acid. TAR is slightly less sensitive than 4-(2-pyridylazo)resorcinol as a reagent for uranium but is more selective.

THE *o*-substituted azo-dyes and bisazo-dyes are among the most sensitive reagents for spectrophotometric determination of uranium in aqueous solution. Heterocyclic azo-dyes with an aromatic nucleus containing a nitrogen atom *ortho* to the azo group also react with the uranyl ion with great sensitivity over a wide range of pH. Of the pyridylazo dyes, the most common, 1-(2-pyridylazo)-2-naphthol (PAN) and 4-(2-pyridylazo)resorcinol (PAR),[1–10] have been used frequently for the spectrophotometric determination of uranium, and their complexation equilibria have been widely studied. PAR is soluble in water and so are its metal chelates, which gives it an advantage over PAN, the metal chelates of which are usually extracted into organic solvents.

Little information is available about the reaction of uranyl ion with thiazolylazo dyes, except for 1-(2-thiazolylazo)-2-hydroxy-4-dimethylaminobenzene,[11] 2-(2-thiazolylazo)-1-hydroxy-5-diethylaminobenzene[12] and 4-(2-thiazolylazo)resorcinol (TAR).[13] Because of its similarity to PAR, TAR aroused our interest in it as a possible analytical and complex-forming reagent. Its reaction with the uranyl ion is described in detail in this paper, and it is shown that TAR is a very useful reagent for the spectrophotometric determination of uranium.

EXPERIMENTAL

Reagents

Uranyl nitrate solution. A stock solution was made by dissolving 49·8 g of uranyl hexahydrate in 100 ml of 1*M* perchloric acid and diluting the solution to 1 l. It was standardized gravimetrically

via triuranium octaoxide, and contained 23·83 mg of uranium/ml. To prevent hydrolysis, the perchloric acid concentration must not fall below 0·1*M*.

TAR. A sample from Lachema, Brno, was recrystallized twice from ethanol in the presence of activated carbon, and dried over calcium chloride hemihydrate to constant weight. The purity of the sample was checked by elemental analysis, ash determination, and potentiometric titration in dimethylformamide–hydrochloric acid medium with chromous chloride.[14] Reagent solutions in ethanol or in dimethylformamide were used, but the concentrations of these solvents in the final solutions never exceeded 4 and 30% v/v respectively.

Control of pH. The pH was adjusted by addition of dilute sodium hydroxide, ammonia, or perchloric acid solutions, and buffers were used only in the determination of uranium. The ionic strength was kept constant at 0·1 by addition of sodium perchlorate.

All chemicals used were analytically pure.

Apparatus

Spectrophotometer. Model SF-4 (USSR) with 1 cm cells.

pH *Meter.* Radiometer PHM 3k, precision ±0·02 pH units.

THE REACTION OF THE URANYL ION AND TAR

At pH $\leqslant$ 3 a soluble red uranyl chelate is formed; the colour of the reagent is yellowish orange in these conditions. At pH $>$ 3·5 the colour of the chelate solution is red-violet, and is intensified by a small excess of ligand or a large excess of metal ion.

The chelating equilibria and the composition and stability of the chelates were studied spectrophotometrically by graphical and numerical analysis of pH–absorbance curves for solutions containing various ratios of metal ion and ligand,[15,16] by the method of continuous variations,[17] by the slope-ratio method,[18] and the mole-ratio method at selected pH values.[19]

All the results in this paper are for solutions containing not more than 4% v/v of ethanol; this amount of ethanol does not affect the results. The pH_k values are valid for 30% v/v dimethylformamide solution and have not been recalculated for true hydronium concentration.

Acid–base equilibria of TAR

The concentrations of the ligand species present in solution (H_3R^+, H_2R, HR^-, R^{2-}) are determined by the acid dissociation constants $pK_{a1} = 0{\cdot}96$, $pK_{a2} = 6{\cdot}23$, $pK_{a3} = 9{\cdot}44$.[20] Only the first two proved to be important, and the wavelengths of maximum absorption were 488 mμ for H_3R^+ and 410–440 mμ for H_2R. The molar absorptivities of these species at 530 mμ were $1{\cdot}15 \times 10^4$ and $2{\cdot}4 \times 10^2$ mole^{-1}. cm^2 respectively.

Absorption spectra of the uranyl chelates

The absorption curves for solutions containing an excess of metal ion, and for equimolar mixtures of the reagents, at pH $<$ 5, have a maximum at 530 mμ and an isosbestic point at 470–475 mμ (Figs. 1 and 2). An additional inflexion in the spectrum of the chelate corresponds to deformation of the ligand absorption maximum at 440 mμ and is similar to that previously found for metal chelates of TAR.[20] For solutions with a small (1- to 5-fold) excess of reagent, the absorption maximum of the chelate is shifted to 540–545 mμ at pH $>$ 5 (after correction for the absorbance due to the free ligand).

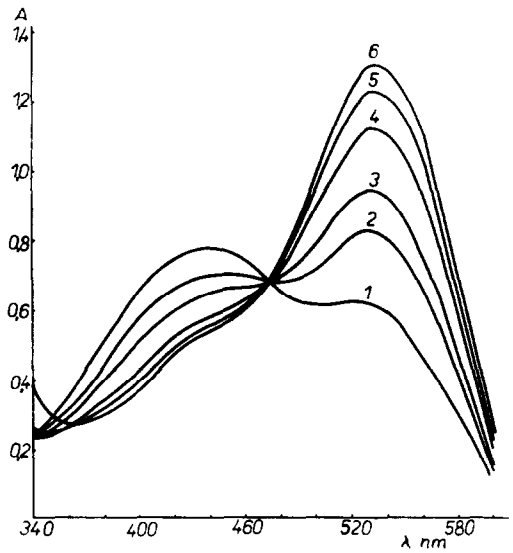


FIG. 1.—Absorption spectra for UO_2^{2+} and TAR in 4% aqueous ethanol.
$C_M = 5{\cdot}0 \times 10^{-5}M$; $C_R = 5{\cdot}0 \times 10^{-5}M$
pH: *1*—2·03; *2*—2·32; *3*—2·55; *4*—3·08; *5*—3·55; *6*—3·98.

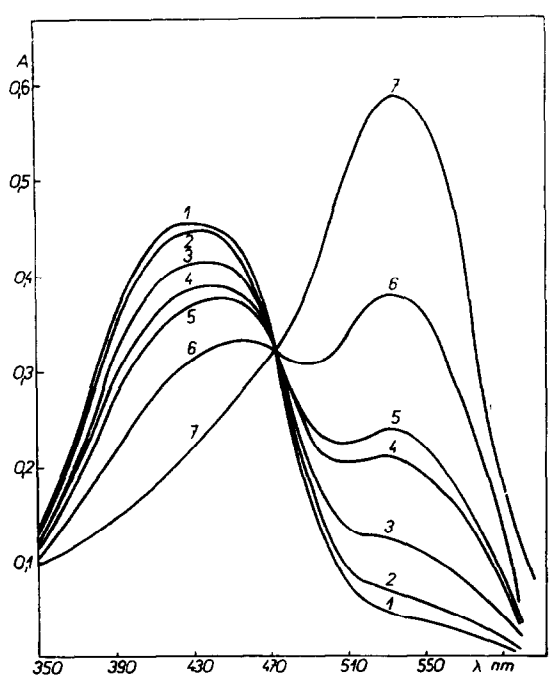


FIG. 2.—Absorption spectra for equimolar UO_2^{2+} and TAR in 20% aqueous ethanol.
$C_M = C_R = 2{\cdot}5 \times 10^{-5}M$
pH_k: *1*—3·26; *2*—3·45; *3*—3·94; *4*—4·10; *5*—4·29; *6*—4·42; *7*—5·65.

pH-Absorbance curves and their interpretation

Previous experience with TAR complexes of metal ions[20] led to the assumption that only 1:1 and 1:2 chelates need be taken into account in interpreting the pH-absorbance curves.

Solutions containing metal ion in excess at pH $\leqslant$ 3·5. Plots of absorbance *vs.* pH give curves which are shifted towards lower pH values as the concentration ratio of metal ion to reagent is increased, and the length of the linear portion of the curves is simultaneously decreased. The curves show a distinct change of slope with increase

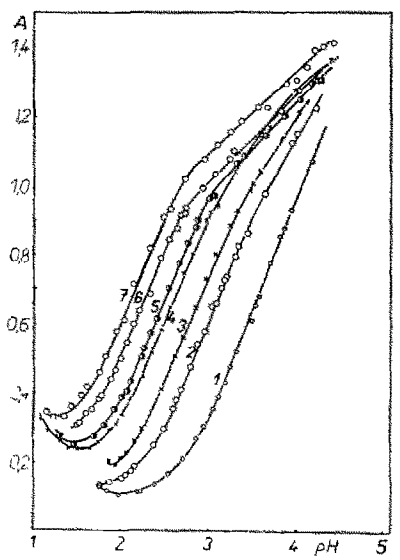


FIG. 3.—pH-Absorbance curves for TAR solutions with excess of UO_2^{2+}, measured at 530 mμ, in 4% aqueous ethanol.
$C_R = 5 \times 10^{-6} M$; C_M/C_R: *1*—4; *2*—10; *3*—16; *4*—25; *5*—50; *6*—80; *7*—100.

in pH if the concentration ratio is high (Fig. 3). It is suggested that above pH 3 the H_3R^+ and H_2R forms of the reagent react according to the equilibria

$$UO_2^{2+} + H_3R^+ \leftrightharpoons UO_2RH^+ + 2H^+ \quad \text{(I)}$$

$$UO_2^{2+} + H_2R \leftrightharpoons UO_2RH + H^+. \quad \text{(II)}$$

To check this suggestion, the curves were analysed graphically by means of the transformations $C_R/A = f[H]^n$ and $\log X = f(\log C_M, \text{pH})$, where C_R and C_M are the analytical concentrations of reagent and metal ion respectively, A is the absorbance and [H] is the hydrogen ion concentration. In addition, the molar absorptivity of the complex and the equilibrium constant were calculated from two points on the curve (absorbances A_1 and A_2) by means of the following set of equations, where ε_{1H} is the molar absorptivity of the complex, ε_{R1} and ε_{R2} are the molar absorptivities of the species H_3R^+ and H_2R respectively, M represents UO_2, the constants are defined by the equations, and the charges are omitted.

H_2R *and* H_3R^+ *are present but only* H_3R^+ *reacts, by equilibrium* (I)

$$k_{12} = \frac{[MRH][H]^2}{[M][H_3R]}$$

$$C_M = [M] + [MRH] \sim [M]$$

$$C_R = [H_3R] + [H_2R] + [MRH]$$

$$A = \varepsilon_{1H}[MRH] + \varepsilon_{R1}[H_3R] + \varepsilon_{R2}[H_2R]$$

$$k_{12} = \frac{a[H]^2}{C_M(\varepsilon_{1H}C_R - A)} \tag{1}$$

$$\varepsilon_{1H} = \frac{a_1[H]^2 A_2 - a_2[H]_1^2 A_1}{C_R(a_1[H]_1^2 - a_2[H]_2^2)} \tag{2}$$

$$C_R/A = \frac{1}{\varepsilon_{1H}} + \frac{a[H]^2}{AC_M k_{12}\varepsilon_{1H}} \tag{3}$$

$$\log \frac{a}{\varepsilon_{1H}C_R - A} = \log k_{12} + \log C_M + 2\text{pH} \tag{4}$$

$$a_n = A_n(1 + K_{a1}[H]_n - C_R(\varepsilon_{R1} + \varepsilon_{R2}K_{a1}/[H]_n). \tag{5}$$

H_2R *and* H_3R^+ *are present but only* H_2R *reacts, according to equilibrium* (II)

$$k_{11} = \frac{[MRH][H]}{[M][H_2R]} = \frac{a[H]}{C_M(\varepsilon_{1H}C_R - A)} \tag{6}$$

$$\varepsilon_{1H} = \frac{a_1[H]_1 A_2 - a_2[H]_2 A_1}{C_R(a_1[H]_1 - a_2[H]_2)} \tag{7}$$

$$C_R/A = \frac{1}{\varepsilon_{1H}} + \frac{a[H]}{AC_M k_{11}\varepsilon_{1H}} \tag{8}$$

$$\log \frac{A - A_0}{\varepsilon_{1H}C_R - A} = \log C_M + \text{pH} + \log k_{11} \tag{9}$$

$$A_0 = \frac{C_R(\varepsilon_{R1}[H] + \varepsilon_{R2}K_{a1})}{[H] + K_{a1}}. \tag{10}$$

H_2R *only is present*

$$C_R = [MRH] + [H_2R]$$

$$A = \varepsilon_{R2}[H_2R] + \varepsilon_{1R}[MRH]$$

$$C_R/A = \frac{1}{\varepsilon_{1H}} + \frac{(A - \varepsilon_{R2}C_R)[H]}{AC_M k_{11}\varepsilon_{1H}} \tag{11}$$

$$\log \frac{A - \varepsilon_{R2}C_R}{\varepsilon_{1H}C_R - A} = \log C_M + \log k_{11} + \text{pH}. \tag{12}$$

The values for ε_{1H} and k_{11} calculated from equations (6) and (7) agree well with other values for these constants (Table I), and confirm that equilibrium (II) occurs at pH $\geqslant$ 1·82 and $C_M = 5 \times 10^{-3}M$. The splitting off of one proton was further confirmed by the straight line obtained for equations (8) and (9) when the value of ε_{1H} calculated from equation (6) (Fig. 4) was used. When equilibrium (I) was considered, the dispersion of values of k_{12} calculated from equation (1) was larger

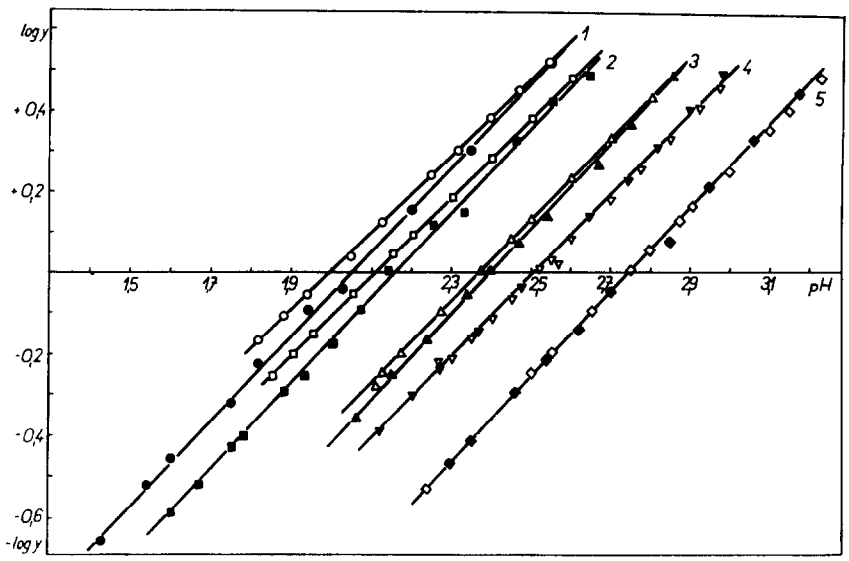


FIG. 4.—Analysis of linear portions of pH-absorbance curves.
$C_R = 5 \times 10^{-5}M$; C_M/C_R: *1*—100; *2*—80; *3*—50; *4*—25; *5*—16
Open points: $y = \log [(A - \varepsilon_{R_2}C_R)/(\varepsilon_{1H}C_R - A)]$
Filled points: $y = \log (A - A_0)/(\varepsilon_{1H}C_R - A)$ where
$A_0 = C_R(\varepsilon_{R1}[H] + \varepsilon_{R_2}K_{a1})/([H] + K_{a1})$.

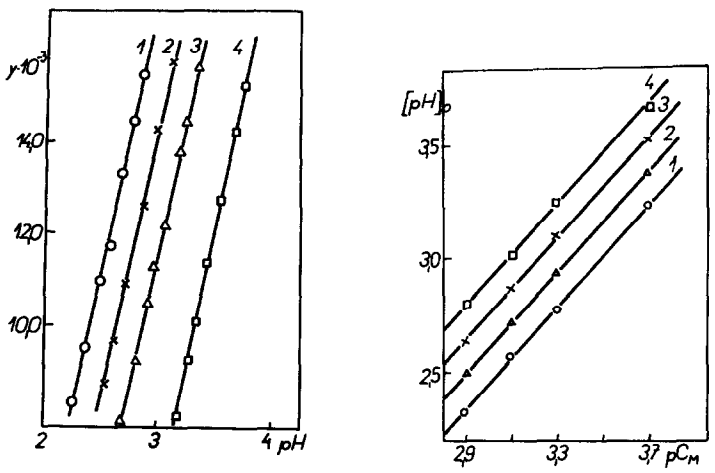
($k_{12} = 0{\cdot}07$–$0{\cdot}21$ for $C_M = 2{\cdot}5 \times 10^{-3} - 5 \times 10^{-3}M$ and $C_R = 5 \times 10^{-5}M$). The existence of H_3R^+ can be neglected at pH > 2·5 and $C_M < 2{\cdot}5 \times 10^{-3}M$ in the interpretation of the pH-absorbance curves. The points on the straight lines for the log functions calculated from equation (11) coincide well with those obtained from equation (9) (Fig. 4). For $C_M > 2{\cdot}5 \times 10^{-3}M$ the deviation of both lines increases rapidly.

By comparison of the family of pH-absorbance curves for various C_M-values, put in the form $pH = f(A - \varepsilon_{R2}C_R)/C_R$ or $pH = \log (A - A_0)/(\varepsilon_{1H}C_M - A)$, a linear plot (Fig. 5a) can be derived for corresponding solutions with equal values of the apparent molar absorptivity:

$$pH_{0i} = (-\log C_M)m/x + \text{constant} \qquad (12)$$

where pH_{0i} represents the pH values for corresponding solutions, m is the number of metal ions bond in the chelate and x is the number of protons split off during chelation.

The results (Fig. 5b) confirm the loss of one proton and the formation of mononuclear MRH at pH 2–3·5, C_M $2{\cdot}9 \times 10^{-3}$–$3{\cdot}7 \times 10^{-3}M$ and C_R $5 \times 10^{-5}M$ (*i.e.*,



(a) (b)

FIG. 5a.—The pH dependence of the apparent molar absorptivity of the uranyl-TAR complex in 4% aqueous ethanol.
$C_R = 5 \times 10^{-5} M$; C_M/C_R: *1*—25; *2*—16; *3*—10; *4*—4 $y = (A - \varepsilon_{R_2} C)/C_R$
FIG. 5b.—Plot of pH $= f(-\log C_M)$ for the corresponding solutions.
$x = (A - \varepsilon_{R_2} C_R)/C_R$.

over the linear lower part of the pH-absorbance curves). In the upper part of the pH-absorbance curves a different equilibrium exists which under certain conditions corresponds to

$$UO_2RH^+ \leftrightharpoons UO_2R + H^+ \qquad \text{(III)}$$

and the equations

$$k_1' = \frac{[MR][H]}{[MRH]}$$

$$C_M \sim [M]$$

$$C_R = [MRH] + [MR]$$

$$A = \varepsilon_{1H}[MRH] + \varepsilon_1[MR]$$

$$k_1' = \frac{(A - \varepsilon_{1H}C_R)[H]}{\varepsilon_1 C_R - A} \qquad (13)$$

$$C_R/A = \frac{1}{\varepsilon_1} + \frac{(A - \varepsilon_{1H}C_R)[H]}{Ak_1'\varepsilon_1} \qquad (14)$$

$$A = \varepsilon_1 C_R - \frac{(A - \varepsilon_1 C_R)[H]}{k_1'} \qquad (15)$$

$$\log \frac{A - \varepsilon_{1H}C_R}{\varepsilon_1 C_R - A} = npH + \log k_1' \qquad (16)$$

where ε, is the molar absorptivity of MR.

For the calculation of ε_1 and k_1' the values of ε_{1H} calculated for the equilibrium (II) postulated as existing for the lower part of the pH curves were used for solutions with

the same concentration of metal ion. The graphical transformations (14) and (15) were most useful for calculating ε_1 simply, and equations (13) and (16) were used for calculation of k_1' (Fig. 6). Consistent values of ε_1 and k_1' were obtained only over limited ranges of pH and metal ion concentration (see Table I): C_R $5 \times 10^{-5}M$; pH 3·40–4·08, C_M $5 \times 10^{-3}M$; pH 3·70–4·50, C_M $4 \times 10^{-3}M$; pH 3·85–4·70, C_M $2{\cdot}5 \times 10^{-3}M$.

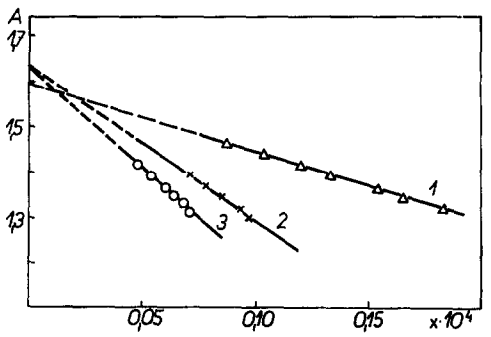


FIG. 6.—Plot of A *vs.* $\varepsilon_1 C_R - (A - \varepsilon_{1H} C_R)[H]/k_1'$ for the second linear portion of the pH-absorbance curves.
$C_R = 5 \times 10^{-5}M$; C_M/C_R: *1*—100; *2*—80; *3*—50.

Below these ranges, MRH is also often present and causes a large deviation in the calculated values, *e.g.*, at pH $< 2{\cdot}7$ and $C_M/C_R = 100$, the value for ε_1, $2{\cdot}33 \times 10^4$, was practically the same as that of ε_{1H}, and a negative value was obtained for k_1', which could have no physical significance. In such a case formation of MRH according to equilibrium (II) must predominate.

Equimolar solutions and solutions with excess of ligand. The pH-absorbance curves for solutions with C_M $2{\cdot}5 \times 10^{-5}$ and C_R $2{\cdot}5 \times 10^{-4}$–$7{\cdot}5 \times 10^{-4}$ were shifted towards lower pH values as the ligand concentration increased, but generally reached a horizontal at pH values >5. Measurements were made at 570 mμ to reduce the absorbance due to the excess of ligand, and corrections were applied for this absorbance. Because of the limited solubility of the ligand in ethanolic medium, 30% v/v aqueous dimethylformamide was used as solvent. From the linear parts of the curves for C_R/C_M ratios of 10, 20 and 30, it was confirmed that equilibrium (II) took place. For this purpose the equations used were

$$C_M = [M] + [MRH]$$

$$C_R = [H_2R] + [MRH] \sim [H_2R]$$

$$C_M/A = \frac{1}{\varepsilon_{1H}} + \frac{[H]}{\varepsilon_{1H} k_{11} C_R} \tag{17}$$

$$\log \frac{A}{\varepsilon_{1H} C_M - A} = \text{pH} + \log C_R + \log k_{11}. \tag{18}$$

The molar absorptivity calculated from the intercept on the graph of equation (17) was used to obtain $\log k_{11}$ from equation (17), Fig. 7. The values of ε_{1H} obtained

agreed well with those for solutions containing excess of metal ion, when the conversion factor $A_{530}/A_{570} = 1{\cdot}08$ was applied.

The higher values of k_{11} were partly influenced by the dimethylformamide present. The MR complex was formed to a negligible extent under the given conditions.

The shape and position of the pH-absorbance curves for nearly equimolar solutions

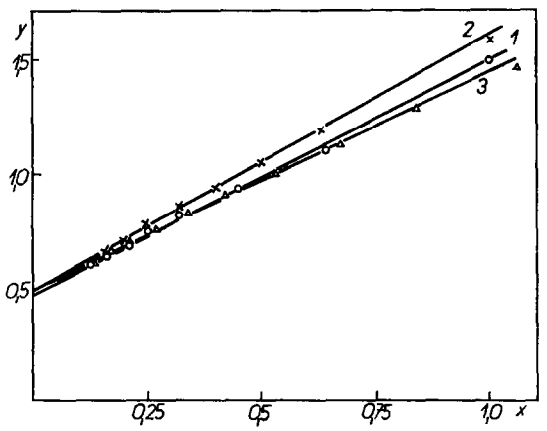


FIG. 7.—Graphical analysis of the rising portion of pH-absorbance curves according to equation (17).
30% aqueous dimethylformamide; 570 mμ
$C_M = 2{\cdot}5 \times 10^{-5}M$; C_R/C_M: *1*—10; *2*—20; *3*—30.

($C_R/C_M \leqslant 6$) were similar to those for a large excess of ligand but the absorbance was about twice as great (Fig. 8). This indicated the existence of the MR species, formed according to the equilibria

$$M + H_2R \leftrightharpoons MR + 2H^+ \quad \text{(IV)}$$

$$M + HR^- \leftrightharpoons MR + H^+ \quad \text{(V)}$$

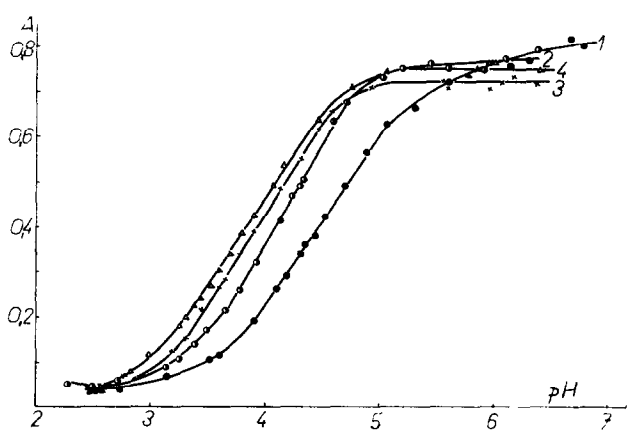


FIG. 8.—pH-Absorbance curves for uranyl-TAR solutions in 8% aqueous ethanol/4% aqueous dimethylformamide.
$C_M = 2{\cdot}5 \times 10^{-5}M$; C_R/C_M: *1*—1; *2*—2; *3*—4; *4*—6.

at pH > 4. The large dispersion of the results for $\varepsilon_1(1{\cdot}15 \times 10^4 - 46{\cdot}1 \times 10^4)$ provides further evidence for the existence of a mixture of MRH and MR species under these conditions.

Other evidence for the 1:1 *complex*

Continuous variation, slope-ratio and mole-ratio plots (Figs. 9, 10, 11) all indicated the existence of a 1:1 complex over the pH range 3·5–7·8. The mole-ratio plot for solutions at pH < 3·3 no longer shows a break on the curves, but this is taken as

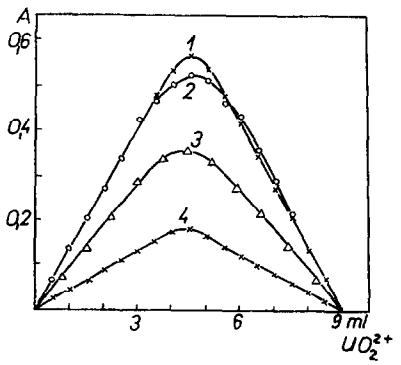


FIG. 9.—Job curves for equimolar solutions of UO_2^{2+} and TAR at 530 mμ.
$C_M = 4{\cdot}5 \times 10^{-5}M$; pH: *1*—7·8 (no buffer); *2*—6·00 (0·2*M* triethanolamine)
$C_M = 3{\cdot}0 \times 10^{-5}M$; pH: *3*—7·8 (no buffer); *4*—6·02 (0·2*M* triethanolamine).

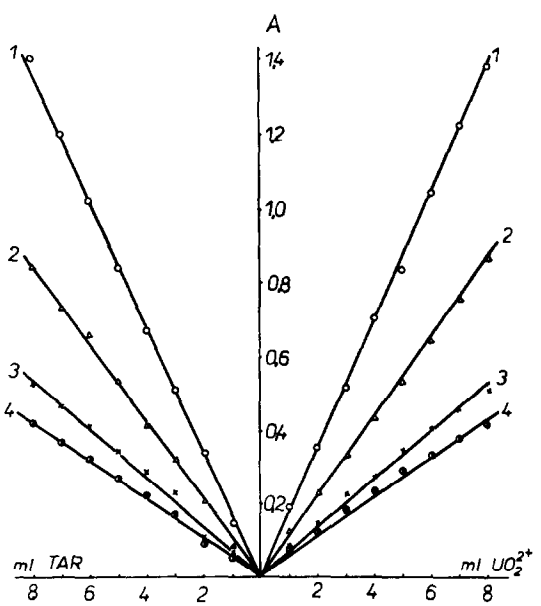


FIG. 10.—Slope ratio plots.
pH 6·67 (0·2*M* triethanolamine); *1*—530 mμ; *2*—570 mμ
pH 3·50 (0·2*M* formate buffer); *3*—530 mμ; *4*—570 mμ.

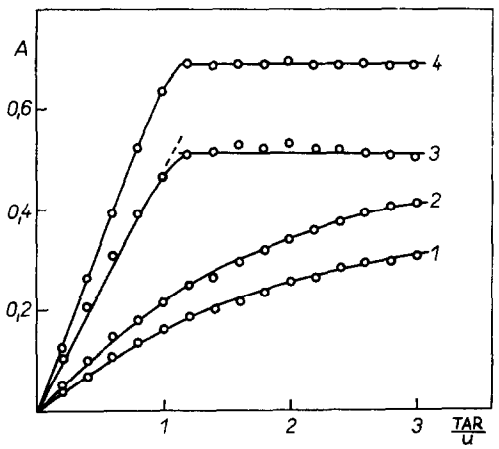


FIG. 11.—Mole ratio plots for increasing concentrations of TAR.
$C_M = 2{\cdot}5 \times 10^{-5}M$; pH 3·63; *1*—570 mμ; *2*—530 mμ;
pH 6·95: *3*—570 mμ; *4*—530 mμ.

evidence of another form of 1:1 complex with a higher absorptivity (occurring when $C_R/C_M > 1$) rather than of the presence of a higher complex.

A green–violet crystalline product was obtained by treating 100 ml of $1{\cdot}25 \times 10^{-3}M$ uranyl nitrate in $1M$ perchloric acid with 50 ml of $1{\cdot}25 \times 10^{-2}M$ TAR in ethanol, and adding $1M$ ammonia dropwise with continuous stirring. The precipitate which appeared at pH 3 was filtered off on a sintered glass crucible, washed with small amounts of ethanol and water, and dried over calcium chloride hemihydrate in a vacuum desiccator. The solid was analysed (found: C 19·6%; H 2·0%; N 7·5%; U 44·1%; H_2O 7·5%; calculated for $UO_2R.2H_2O$: C 20·5%; H 1·7%; N 8·0%; U 45·2%; H_2O 6·8%) and the ratios U:C and U:N were 1:8·8 and 1:2·9, compared with 1:9 and 1:3 expected theoretically. The compound strongly adsorbs water, so the water content is always higher than the theoretical value. There was no evidence for the formation of a 1:2 complex in the solid state.

*Constants for the uranyl-*TAR *chelate*

We may summarize the various equilibrium constants for the system:

$$k_{11} = [MRH][H]/[M][H_2R]$$

$$k_{12} = [MRH][H]^2/[M][H_3R]$$

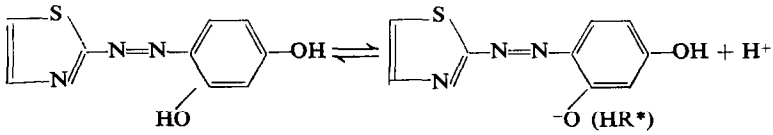
$$k_1' = [MR][H]/[MRH]$$

$$k_{12} = k_{11}.K_{a1}$$

$$K_{1H} = [MRH]/[M][HR^*] = k_{11}/K_{a2}^*$$

$$K_1 = [MR]/[M][R] = k_1'K_{1H}/K_{a3}^*$$

where K_{a2}* is the dissociation constant for the hypothetical dissociation



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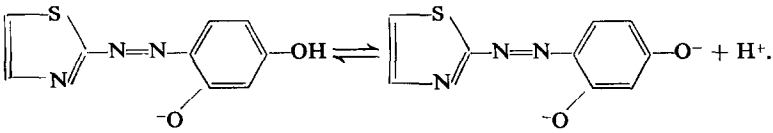

These hypothetical constants are required for the evaluation of K_{1H} and K_1 because in the formation of the complex MRH the proton of the *o*-hydroxy group is displaced, whereas it is the *p*-hydroxy group that dissociates first in the absence of a complex-forming cation. It is not possible to measure the values of these "reversed" dissociation constants, and for simplicity it is assumed[21,22] that they have the same values as the normal constants, *i.e.*, $pK_{a2}^* = pK_{a3}$ and $pK_{a3}^* = pK_{a2}$.

The values for particular equilibrium constants and absorptivities are given in Table I. There is good agreement between the values obtained by different methods. The values for the other constants then become: $\log k_{12} = -0{\cdot}65$; $\log K_{1H} = 9{\cdot}8$; $\log K_1 = 11{\cdot}35$.

TABLE I.—MOLAR ABSORPTIVITIES AND EQUILIBRIUM CONSTANTS

MRH $\varepsilon_{1H} \times 10^{-4}$	MR $\varepsilon_1 \times 10^{-4}$	$\log k_{11}$	$\log k_1'$
2·4; 2·3 (7)	$3{\cdot}4_5$; 3·4; 3·3 (14)	0·28 (6)	−4·5 (13)
$2{\cdot}4_5$; 2·3; $2{\cdot}3_4$; 2·4 (10)	3·3 (15)	0·30 (11)	−4·5 (16)
2·3 (17)	3·3*	$0{\cdot}28_6$ (9)	
	$3{\cdot}3_5$†	0·34; 0·40 (18)‡	

Numbers in brackets are those of the equations used.

The results for equations (6), (9), (11), (13) and (16) are the means of 3, 5, 5, 4 and 4 values respectively, for various excesses of ligand and metal ion.

Absorbances were corrected for the absorbance of excess of ligand.

* Calculated by $\varepsilon_1 = A/C_R$ or $\varepsilon_1 = A/C_M$ from Job plots at pH > 6 with excess of ligand or metal ion (mean of 9 values).

† From linear plots of $A = f(C_R)$ for solutions with excess of metal ion at pH 6·95 (slope ratio method).

‡ Values obtained for solutions in 30% v/v aqueous dimethylformamide.

The agreement of the values for the molar absorptivity calculated from Job plots, slope-ratio plots, pH-absorbance curves and equations (14) and (15) is further evidence that only the MR species is formed at pH > 6, and not MR_2.

SPECTROPHOTOMETRIC DETERMINATION OF URANIUM

Of the 1:1 chelates formed under various conditions, the UO_2R complex is the most suitable for spectrophotometric use. Although this complex is the sole species formed at pH > 5 if the ligand is present in excess, pH 7·5–8 was chosen because at this pH the complex is formed quantitatively in the presence of only a small excess of ligand and several interfering ions can be masked.

Reaction conditions

Sodium acetate, triethanolamine, tris(hydroxymethyl)aminomethane and urotropine were used as buffers, for the pH range 6–8. None of them influenced the absorbance of the chelate when they were present in 0·2–0·4*M* concentration. For further work 0·1*M* triethanolamine was used; a 1*M* stock solution was adjusted to pH 7·5–8 by addition of perchloric acid.

For determination of 20–120 μg of uranium, 5 ml of $4 \times 10^{-4}M$ TAR in 96% ethanol or 0·1*M* ammonia were used. If the ammoniacal reagent was used, a few drops of 0·1*M* perchloric acid were added until the red colour of the solution changed to yellow, and then 5 ml of 96% ethanol were added to keep the reagent in solution.

Variation of the ionic strength over the range 0·1–0·3 (by addition of sodium perchlorate) was without influence on the absorbance. The absorbance increases slightly in the first 60 min and then begins to decrease. The optimal time for measuring the absorbance is 0–10 min after the solution has been prepared. Beer's law is obeyed over the range 0·4–4·8 ppm of uranium at pH 3–8 in the absence of a buffer or at pH > 6 in the presence of 0·2*M* triethanolamine, 0·04*M* urotropine or 0·02*M* sodium acetate.

The molar absorptivity calculated from several points on the calibration curve was $3{\cdot}30 \times 10^4$ (mean of 9 values), in good agreement with the values given in Table I.

Influence of masking agents

Table II shows the effect of various common masking agents. Carbonate and oxalate were found to interfere strongly. Fluoride, cyclohexanediaminetetra-acetic

TABLE II.—EFFECT OF SOME MASKING AGENTS ON THE DETERMINATION OF 60 μg OF URANIUM

Masking agent	Concentration ratio agent/uranium	Relative error in determination, %
EDTA	20	−2·0
CHDTA	3000	−0·8
Sodium fluoride	5000	+3·0
5-Sulphosalicyclic acid	3100	−3·0
Sodium thiosulphate	16000	−0·7
Sodium acetate	6000	+3·3
Potassium sodium tartrate	400	−5·8
Diammonium hydrogen phosphate	420	+2·8
Hydrogen peroxide	4200	−4·4

acid (CHDTA) and 5-sulphosalicylic acid are very useful masking agents for a number of interfering ions, and the mixture of them recommended by Florence and Farrar[9] was used in this work. Even when a large excess of this mixture was added there was less than 3% change in the absorbance of the uranyl–TAR complex. The mixture used contained 25 g of cyclohexanediaminetetra-acetic acid, 2·5 g of sodium fluoride and 65 g of 5-sulphosalicyclic acid dissolved in water to give a solution which was neutralized with ammonia (1 + 1), filtered, adjusted to pH 7·5–8 with dilute ammonia, and diluted to 1l.

Procedure

To the slightly acid sample solution (in a 50 ml volumetric flask) containing 20–120 μg of uranium add 10 ml of masking mixture, 5–6 drops of phenolphthalein

TABLE III.—DETERMINATION OF 60 μg OF URANIUM IN THE PRESENCE OF VARIOUS IONS

Salt added	Concentration of metal ion, *mg/ml*	Relative error of determination, %
$Al(NO_3)_3$	0·111	+1·3
$MnSO_4$	0·130	+0·7
$Cd(NO_3)_2$	1·168	+6·6
$Bi(ClO_4)_3$	0·105	+2·3
$Fe(Clo_4)_3$	0·326	−4·4
$Be(NO_3)_2$	0·053	−5·8
$InCl_3$	0·186	+1·3
$GaCl_3$	0·049	+0·7
$Th(NO_3)_4$	0·154	+2·8
$La(ClO_4)_3$	0·300	+5·7
$Y(ClO_4)_3$	0·063	+1·3
$Dy(ClO_4)_3$	0·107	+2·8
$Yb(ClO_4)_3$	0·099	−4·3
$Pr(NO_3)_3$	0·220	−2·8
$Zr(NO_3)_4$	0·114	+2·2
$VOSO_4$	0·010	+2·9
$Hg(NO_3)_2$	0·104	+1·3
$CuSO_4$	0·194	+2·8
$Co(NO_3)_2$	0·024	+2·2
$Ni(NO_3)_2$	0·057	−2·8
$Zn(NO_3)_2$	0·735	−2·8
K_2CrO_4	0·027	+3·0
$Ce(SO_4)_2$	0·018	+3·5
Na_2MoO_4	2·70	−4·4
Na_2WO_4	0·488	−2·8

and first ammonia until a pink colour appears and then just enough 1*M* perchloric acid to discharge the colour. Then add 5 ml of $4{\cdot}0 \times 10^{-4}M$ TAR in 96% ethanol, and 5 ml of 1*M* triethanolamine buffer, pH 7·5–7·8. Dilute the mixture to the mark, mix, and measure the absorbance within 10 min in 1-cm cells at 530–545 mμ against a reagent blank of the same composition and pH. The sensitivity is 0·072 μg/cm^2 for an absorbance of 0·01, and the relative error is less than 2%.

Effect of various ions

Table III shows the effect of various ions on the determination of uranium by the procedure given.

Acknowledgement—Thanks are due to V. Svoboda who supplied the sample of TAR.

Zusammenfassung—Das Uranylion bildet nur 1:1-Chelate mit 4-(2-Thiazolylazo)resorcin (TAR) in Lösung, $UO_2(TAR)H^+$ bei pH < 3 und $UO_2(TAR)$ bei pH > 3,5. Der zuletzt genannte Komplex kann auch bei pH > 3 gefällt werden. Die quantitative Bildung von $UO_2(TAR)$ bei pH 7,5–7,8 in Lösungen, die einen kleinen Reagensüberschuß und Triäthanolamin als Puffer enthalten, kann zu empfindlicher spektrophotometrischer Bestimmung von Uran dienen. Mehrere störende Ionen können mit einer Mischung von Natriumfluorid, Cyclohexandiamintetraessigsäure und 5-Sulfosalicylsäure maskiert werden. TAR ist als Uranreagens etwas weniger empfindlich als 4-(2-Pyridylazo)resorcin, aber selektiver.

Résumé—L'ion uranyle ne forme que des chélates 1:1 avec le 4-(2-thiazolylazo) résorcinol (TAR) en solution, $UO_2(TAR)H^+$ se formant en-dessous de pH 3 et $UO_2(TAR)$ au-dessus de pH 3,5. Le dernier complexe peut aussi être précipité à pH 3. On peut utiliser la formation

quantitative de UO_2(TAR) à pH 7,5–7,8 en solutions contenant un faible excès de réactif et un peu de triéthanolamine comme tampon pour le dosage spectrophotométrique sensible de l'uranium. On peut dissimuler différents ions gênants par un mélange de fluorure de sodium, acide cyclohexanediaminotétracétique et acide 5-sulfosalicylique. Le TAR, en tant que réactif de l'uranium, est légèrement moins sensible que le 4-(2-pyridylazo) résorcinol, mais il est plus sélectif.

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DETERMINATION OF ALUMINA FILM THICKNESS BY ALPHA PARTICLE SCATTERING

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Summary—The scattering of accelerated alpha particles has been used to determine the surface oxide film thickness of anodized aluminium. The measurements were based on determining the difference between the energy of an alpha particle cattered from the surface oxide layer and that from the underlying metal. Films ranging in thickness from 10 to 130 μg/cm^2 were analysed non-destructively with a relative standard deviation of 3·5%. The average time for an analysis was 30 min with an incident beam current of up to about 1 μA.

PREVIOUS work[1] has shown that use may be made of semiconductor detectors to measure the energy spectrum of elastically scattered alpha particles for qualitative and quantitative analysis of surface films. The method was applied to the measurement of surface concentrations of heavy metals deposited on backing materials with lower atomic number.[2] This work extends the technique to the determination of surface concentrations of light elements. Oxide films have been analysed on aluminium.

Theory

The Rutherford differential scattering cross section, $d\sigma/d\Omega$ for single scatter of a charged particle through a centre-of-mass angle θ, moving with non-relativistic velocities, is given[3] by

$$\frac{d\sigma}{d\Omega} = \frac{b^2}{16 \sin^4 \theta/2} \text{ cm}^2 \text{ . atom}^{-1} \text{ . steradian}^{-1}, \quad (1)$$

where b, the distance of closest approach, is given by

$$b = \frac{Z_1 Z_2 e^2}{E} \text{ cm}. \quad (2)$$

Z_1 and Z_2 are respectively the atomic numbers of the bombarding charged particle and the target nucleus, e is the electronic charge and E the incident energy of the charged particle.

After scatter, the energy of the scattered particle, E', is given by

$$\frac{E'}{E} = 1 - 2(1 - \cos \theta) \frac{M_1 M_2}{(M_1 + M_2)^2} \quad (3)$$

where M_1 and M_2 respectively are the masses of the incident and target nuclei.

When scattering occurs within the target material, the particle will lose energy by

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ionization and excitation along its inward and outward paths, and by scattering at a particular depth i. The energy of the particle at the detector, E_{di}, is given by

$$E_{di} = [E - \Delta E_i]\left[1 - 2(1 - \cos\theta_i)\frac{M_1 M_2}{(M_1 + M_2)^2}\right] - \Delta E_i' \tag{4}$$

where the energy ΔE_i lost along the inward path length S_{1i} and $\Delta E_i'$ along the outward path length S_{2i} are obtained from

$$\Delta E_i = \int_0^{S_{1i}} \frac{dE}{dx}\, ds \quad \text{and} \quad \Delta E_i' = \int_0^{S_{2i}} \frac{dE'}{dx}\, ds. \tag{5}$$

When a charged particle beam is scattered off a monolayer target containing two components with nuclidic masses ${}^1M_2$ and ${}^2M_2$ in fractional concentrations n_1 and n_2 atoms/cm^2 respectively, the energy spectrum of the scattered particles measured at a selected laboratory angle θ_L will consist of two normal distributions about energies E_1' and E_2' respectively, provided the difference between these two energies is appreciably greater than the resolution of the detecting system which determines the width of each peak. The energies E_1' and E_2' may be obtained from equation (3) in which the corresponding centre-of-mass angle is used. The centre-of-mass angle is given by

$$\theta = \theta_L + \arcsin\left(\frac{M_1}{M_2}\sin\theta_L\right). \tag{6}$$

The area under each peak, and consequently the peak height, is proportional to the product of the fractional concentration of the component and its scattering cross-section.

With a thick target, each layer may be considered to yield a similar set of peaks in the energy spectrum of the scattered particle, but the energy is degraded according to equation (4). Any observed spectrum will consist of the sum of the spectra of the layers and should provide information about the atomic mass M_2 and the number of atoms per unit area of beam (n) of each constituent element.

Selection of experimental conditions

One of the factors determining resolution is the variation of the scattered energy E' with unit increase in M_2. The mass sensitivity, $S(M_1)$, can be obtained by differentiating equation (3) with respect to M_2 at a constant value of the scattering angle for each type of bombarding particle M_1.
Thus

$$S(M_1) = \frac{\partial}{\partial M_2}\left(\frac{E'}{E}\right)_{\theta_L} = \frac{2M_1(1 - \cos\theta)(M_2 - M_1)}{(M_1 + M_2)^3} + \frac{2M_1 \sin\theta \tan(\theta - \theta_L)}{(M_1 + M_2)^2} \tag{7}$$

for constant laboratory angle θ_L. Curves for the mass sensitivity with respect to protons, alpha particles and nitrogen ions are given in Fig. 1 for $\theta_L = 135°$. From this figure it is clear that alpha particles give the best resolution in the analysis of alumina films.

The criterion for selecting a suitable scattering angle was that the energy difference between particles scattered from aluminium and from oxygen should be as great as possible. Figure 2 shows the variation of E'/E with laboratory angle for aluminium

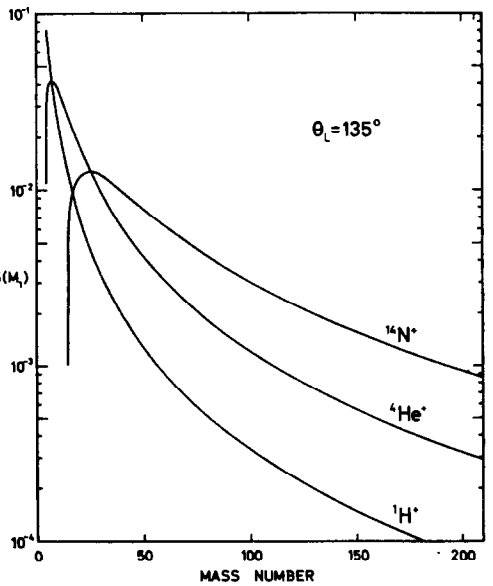

FIG. 1.—Mass sensitivity for protons, alpha particles and nitrogen ions scattered through a laboratory angle of 135°.

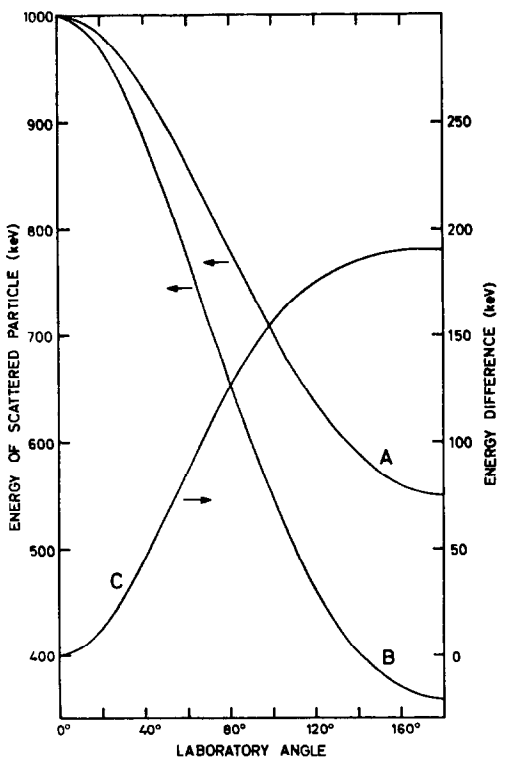

FIG. 2.—Effect of variation of scattering angle on the energy of the alpha particles scattered from aluminium (A), oxygen (B) and the difference between them (C). Incident energy = 1·00 MeV

and for oxygen. In the same figure, the energy difference between particles scattered from aluminium and oxygen at the same depth is shown as a function of the scattering angle for an incident beam of 1 MeV. Although the energy difference increases, there is relatively little change for angles greater than 135°. Accordingly this angle was selected.

The bombarding energy was chosen on the criterion that the rate of energy loss of the alpha particles should be as large as possible, within the alumina, so that penetration into the aluminium metal should be minimized. The lower the energy E, the lower the penetration, but the Van de Graaff accelerator could not give a stable beam much below 0·6 MeV. However, at this energy, the separation between E_1' and E_2' was not sufficiently large. The energy was thus stepped up to 1 MeV as a compromise between better resolution and poorer penetration properties.

EXPERIMENTAL

Apparatus

The 5·5 MeV Van de Graaff accelerator at the Southern Universities Nuclear Institute provided the beam of singly charged helium-4 ions of 1 MeV with energy spread of ± 1 keV. In all cases the incident beam was collimated to a cross-sectional area of 5×10^{-3} cm². With currents of up to 1 μA no vaporization could be detected from the targets, because of the refractory nature of alumina. When gold was used for calibration, lower currents were used to prevent gold volatilization.

The scattering chamber with the collimation for the incident beam was the same as described previously.[2] The detector assembly consisted of a surface barrier silicon solid state detector[4] with an active area of 0·2 cm², mounted 12·7 cm from the point of scatter. When required, collimators could be inserted in the scattered beam to reduce background from multiply scattered alpha particles.

The target assembly allowed for two 17 mm metal plates to be mounted for analysis. An aperture between them enabled the beam to be passed directly to a Faraday cup for current measurement. The entire target assembly was insulated and connected to a current integrator.[5]

Measurement and resolution

Pulses from the solid state detector were amplified and transmitted to a multichannel analyser on which the entire observed spectrum was recorded. The resolution of the detector, as measured by the full width at half the height of the spectrum peak obtained from the 5·48 MeV alpha particles from americium-241 was never more than 55 keV.

Calibration of the measuring system

The scattering of alpha particles at $\theta_L = 135°$ was measured for gold, aluminium and carbon. On adjustment of the scattering angle to centre-of-mass co-ordinates, the three energies obtained from equation (3) gave a straight line calibration. With thick targets the inflection point of the plateau edge in the spectrum was taken as E'.

Preparation of alumina targets

Alumina films of different thicknesses were prepared by anodizing one side of an aluminium foil in 3% w/v triammonium citrate at voltages ranging from 20 to 280 V. The foils were washed in water and stored in vacuum desiccators till required.

Standardization of film thicknesses

Previous work[6–10] has shown that the thickness of alumina formed during anodization is a linear function of the voltage. The mean value of the proportionality constant was accepted as 0·478 μg of alumina/V. As a check on the alumina film thickness, the oxygen content of anodized films was determined by helium-3 activation and measurement of the induced fluorine-18 activity.[11]

RESULTS AND DISCUSSION

Energy spectra of alpha particles scattered from untreated aluminium and from anodized aluminium with thin and thick layers of oxide are shown in Fig. 3. As was expected, the energy spectrum for a thin oxide layer showed a single plateau, caused

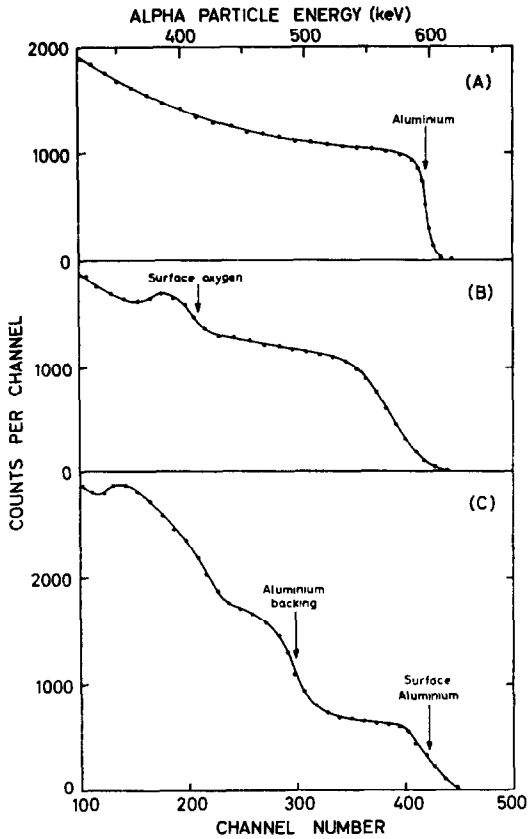

FIG. 3.—Energy spectra of alpha particles scattered from untreated aluminium (A), and from anodised aluminium with thin (B) and thick (C) layers of oxide. $\theta_L = 135°$, $E = 1{\cdot}00$ MeV, counted for 30 min.

by alpha particles scattered from a thick layer of aluminium, with a broadened peak corresponding to a much thinner layer of oxygen, superimposed on the plateau. It was found that the calculated value of E' for oxygen (0·417 MeV) agreed with the maximum energy of particles scattered from oxygen (as measured by the inflection point of the protruding peak in the spectrum). However, the inflection point of the plateau was found to be at a somewhat lower energy than that calculated for E' for aluminium (0·598 MeV). Examination of the same spectrum showed that the leading edge of the spectrum did not fall to zero as rapidly as was the case with unanodized aluminium foil. With increasing target thickness the difference between the measured and the calculated energies corresponding to aluminium increased. At the same time the number of counts recorded in the leading edge of the spectrum increased with thickness until the leading edge resolved into another plateau, the energy of the inflection point of which corresponded exactly to the energy of alpha particles scattered from surface layers of aluminium. An example of a spectrum with three plateaux is shown in Fig. 3C.

The inflection point of the edge of the intermediate step in the energy spectrum

corresponding to an energy intermediate between that of oxygen and aluminium, was found to vary with the thickness of alumina and was displaced to lower energies with increasing thickness of the alumina. If the energy measured from scatter occurring from aluminium in the last layer of alumina is E_{d1} [see equation (4)], then the maximum energy measured from scatter at the surface of the aluminium metal, $E_{d(1+1)}$, is related to $(S_1 + S_2)$, the total path length of the alpha particle in alumina. The difference between the energy of a particle scattered from a surface atom of aluminium in alumina and $E_{d(1+1)}$, represents the total energy loss of the particle in alumina. Thus the energy $E_{d(1+1)}$, corresponding to the inflection point of the intermediate plateau can serve as a measure of alumina thickness.

The crystal structure of aluminium metal is cubic close packed with a unit cell of 4·04 Å and an average distance between aluminium atoms[13] of 2·86 Å. In the case of γ-alumina, the unit cell[12] is 7·90 Å with oxygen atoms in cubic close packing. The 24 aluminium atoms are randomly situated in 8 of the 64 sites which have oxygen tetrahedrally arranged around them and 16 of the 32 sites where oxygen is octahedrally arranged. The shortest distance between two octahedrally surrounded aluminium atoms is about 2·8 Å, while between tetrahedrally and octahedrally surrounded ones it is 3·1 Å and between tetrahedrally surrounded atoms, about 3·4 Å. The overall effect is that the average distance between aluminium atoms in alumina is appreciably greater than in aluminium metal. The difference in intensity of the alpha particles scattered from within the alumina and those from the aluminium metal, and hence the appearance of the intermediate plateau in the energy spectrum, is attributed to the increased concentration of aluminium atoms per unit area of the beam.

Recent work[14–17] has indicated that energetic ions could penetrate ordered crystalline structures along favoured crystallographic directions without appreciable loss of energy. Thus, for an alumina layer which is deposited as an ordered crystal and on which the alpha particle irradiation beam is incident in precisely the favoured direction, scattering data could lead to a low result. However, as anodization is unlikely to lead to ordered crystals and because the thickness of the film is obtained from the difference in energy between particles scattered from *surface* aluminium atoms of alumina and *surface* aluminium atoms from the underlying metal, this effect can be neglected. Alternatively, penetration of the underlying metal by channelling would result in a small change of the number of particles scattered from *within* the aluminium, which would again have little bearing on the analysis.

A calibration curve of the maximum energy of an alpha particle scattered from the aluminium metal as a function of alumina thickness is given in Fig. 4. The energy error flags shown in Fig. 4 refer to the errors involved in determining the inflection point in the spectrum, while the thickness error flags refer to the standardization errors from the determination of oxygen by helium-3 activation.

The results of a typical series of analyses are shown in Table I. The values of the known thickness in the table were obtained from activation analysis. The precision of the method as given by the relative standard deviation was found to be 3·5%, while the statistical scatter of results and the mean error indicated no bias. It should be noted that the relative standard deviation included errors from activation analysis, the results of which were assumed to be absolute for purposes of calculation. Because the precision of the standardization by activation analysis[11] or by the variation of film thickness with the anodizing voltage[6–10] is about the same as the value of 3·5% found

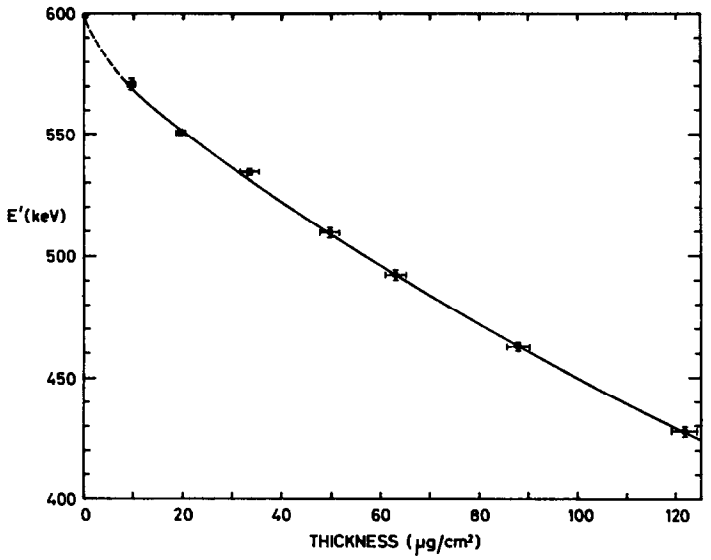

FIG. 4.—The variation of the maximum energy of alpha particles scattered from aluminium metal with thickness of alumina film.

TABLE I.—SOME ANALYSES OF ALUMINA LAYERS ON ALUMINIUM

Sample number	*E, keV*	Thickness, $\mu g/cm^2$			Relative error, %
		Found	Known	Difference	
1	559	15·54	14·34	+1·20	+8·37
2	557	16·83	16·73	+0·10	+5·98
3	549	21·84	22·94	−1·10	−4·80
4	543	25·62	26·29	−0·67	−2·55
5	539	28·49	29·64	−1·15	−3·88
6	520	41·78	41·11	+0·67	+1·63
7	502	55·45	54·01	+1·44	+2·67
8	497	59·37	57·84	+1·53	+2·65
9	490	65·25	67·40	−2·15	−3·19
10	480	73·04	72·18	+0·86	+1·19
11	476	76·48	77·44	−0·96	−1·24
12	438	110·75	110·42	+0·33	+0·30

Mean error +0·00833 $\mu g/cm^2$
Mean relative error +0·59%
Relative standard deviation ±3·5%

here, it may be deduced that the method of alpha particle scattering is, at worst, as precise as these two methods.

Applications

The method of alpha particle scattering affords a convenient method for measuring oxide films on aluminium from 10 to about 150 $\mu g/cm^2$ by the technique of determining the energy lost by the incident and scattered particles passing through the film. The method may be extended to thin films of light elements on metals and heavy elements. For thicker films the incident energy of the alpha particle may be increased,

thus increasing the range of applicability of the method without appreciable loss of sensitivity.

In corrosion studies the oxide film on iron may be measured *in situ*, without having to float the oxide film off the underlying metal.[18] Alternatively films of iron oxide floated off corroded surfaces may be analysed for homogeneity.

Acknowledgements—One of us (D. O. P.) thanks the South African Atomic Energy Board for permission to include his work in this report. Another of us (H. F. R.) thanks the South African Council for Scientific and Industrial Research for a bursary enabling him to take part in this work, which forms part of his Master's thesis accepted by the Chemistry Department, University of Stellenbosch. The assistance of O. B. E. Teuteberg with the construction of some apparatus and of P. A. d'A. Hill with the activation analysis, is gratefully acknowledged.

Résumé—On a utilisé la diffusion des particules alpha accélérées pour déterminer l'épaisseur du film superficiel d'oxyde sur l'aluminium oxydé anodiquement. Les mesures sont basées sur la détermination de la différence entre l'énergie d'une particule alpha diffusée par la couche d'oxyde superficiel et celle d'une particule diffusée par le métal sous-jacent. On a analysé de façon non destructive des films d'épaisseur comprise entre 10 et 130 $\mu g/cm^2$ avec un écart type relatif de 3,5%. Le temps moyen nécessité par une analyse est de 30 min, avec une intensité de faisceau incident allant jusqu'à 1 μA environ.

Zusammenfassung—Die Streuung beschleunigter Alphateilchen wurde benutzt, um die Dicke des Oxydfilms auf der Oberfläche anodisch oxydierten Aluminiums zu bestimmen. Die Messungen beruhten auf der Bestimmung der Differenz der Energie eines Alphateilchens, das einerseits an der oberflächlichen Oxydschicht, andererseits am darunterliegenden Metall gestreut wurde. Filme der Dicke 10–130 $\mu g/cm^2$ wurden zerstörungsfrei mit einer relativen Standardabweichung von 3,5% analysiert. Die durchschnittliche Zeit für eine Analyse betrug 30 min mit einer Stromstärke des auftreffenden Strahls bis etwa 1 μA.

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ANALYSIS OF ZONE-MELTED ULTRA-PURE ORGANIC COMPOUNDS*

A NEW QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS METHOD

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Summary—A method for the rapid quantitative determination of impurities in ultra-pure organic compounds is described. It is based on the difference in slopes of the curves obtained when the difference in temperature between the sample and a reference shield is plotted against time. The results are compared with those obtained by thermal analysis.

IN the past, differential thermal analysis (DTA) has been used qualitatively to evaluate the purity of samples by comparison of the DTA curves for the materials in various states of purity.[1,2] Such evaluations have relied heavily on the theory of dynamic methods of thermal analysis. These methods are not based on the changes occurring during phase transitions or chemical reactions (as other applications of DTA are often based) but rather on Newton's law of heating and cooling, applied to the premelting phase of a solid or to the cooling molten phase. The influence of impurities on the premelting phase may be related to the equations associated with the lowering of the melting point. It can easily be shown from two fundamental equations that not only the lowering of the melting point but also all temperatures in the premelting phase are proportionately affected by the concentration of the impurity, which may be measured by DTA methods.

Herington[1] has recently developed two procedures; a quantitative thermal analysis procedure and a very rapid qualitative DTA method. In the latter, he uses a copper block, alongside the sample, to act as a "shield" or temperature reference. When the temperature difference between sample and shield is plotted against time for a series of samples of different purity, the slopes of the curves give a rough estimate of the purity. We have adapted Herington's method to permit the determination of impurities in ultra-pure organic substances. Methods for increasing the sensitivity of thermal analysis methods have been published separately[3] and only those parts needed for standardizing the DTA procedure will be given here. The theory and experiments for both the premelting and the cooling phases have been completed; as the theory and procedures are similar for both phases only the premelting phase will be considered here.

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THEORY

The slope of the curve of the temperature difference between shield and sample plotted against time can be related to the mole % of impurity by the equation

$$\frac{\Delta(\Delta T_1)}{\Delta(\Delta T_2)} = \frac{Gn_1}{n_1 + n_2} \tag{1}$$

where $\Delta(\Delta T_1)$ and $\Delta(\Delta T_2)$ are the slopes of the temperature difference curves of two samples, G is a constant to be theoretically derived, n_1 is the mole % of impurity in the original sample, and n_2 is the mole % of impurity added to obtain the second sample. The method is a mathematical refinement of Herington's procedure,[1] making it quantitative. Herington's final equation[1] is used as a starting point:

$$\frac{\Delta T_1}{\Delta T_2} = \frac{n_1}{n_1 + n_2}. \tag{2}$$

Let $\Delta T_1 = (T_B - T_A)$, $\Delta T_2 = (T_D - T_C)$, $\Delta(\Delta T_1) = [(T_{AS} - T_A) - (T_{BS} - T_B)]$ and $\Delta(\Delta T_2) = [(T_{CS} - T_C) - (T_{DS} - T_D)]$, where T_A and T_B are the temperatures of sample 1 at times A and B respectively, T_{AS} and T_{BS} are the corresponding temperatures of shield 1, and T_C *etc.*, refer similarly to sample 2.

Then

$$\Delta(\Delta T_1) = (T_B - T_A) - (T_{BS} - T_{AS}) = \Delta T_1 - \Delta T_{1S} \tag{3}$$

and

$$\Delta(\Delta T_2) = (T_D - T_C) - (T_{DS} - T_{CS}) = \Delta T_2 - \Delta T_{2S}. \tag{4}$$

If plots of ΔT_1 against ΔT_{1S} and of ΔT_2 against ΔT_{2S} are linear and pass through the origin, then

$$\Delta T_1 = K_1 \Delta T_{1S};\ \Delta T_2 = K_2 \Delta T_{2S} \tag{5}$$

where K_1 and K_2 are the slopes of these plots. Substitution of equation (5) in equation (3) yields

$$\Delta(\Delta T_1) = \Delta T_1 - \Delta T_1/K_1 \tag{6}$$

and similarly

$$\Delta(\Delta T_2) = \Delta T_2 - \Delta T_2/K_2. \tag{7}$$

Then

$$\frac{\Delta(\Delta T_1)}{\Delta(\Delta T_2)} = \frac{K_2}{K_1}\frac{\Delta T_1}{\Delta T_2}\frac{(K_1 - 1)}{(K_2 - 1)} \tag{8}$$

and substitution from equation (2) gives

$$\frac{\Delta(\Delta T_1)}{\Delta(\Delta T_2)} = \frac{K_2}{K_1}\frac{(K_1 - 1)}{(K_2 - 1)}\frac{n_1}{(n_1 + n_2)} \tag{9}$$

which yields equation (1) if

$$G = K_2(K_1 - 1)/K_1(K_2 - 1). \tag{10}$$

EXPERIMENTAL

Apparatus

A Leeds and Northrup (L & N) 9835–B stabilized d.c. microvolt amplifier and a Speedomax H continuously adjustable Azar recorder were used for the DTA measurements. The microvolt amplifier is a null-balance instrument suitable for measuring the voltage output of thermocouples. It can be used as a preamplifier in combination with the recorder to give increased sensitivity over long or short test periods.

The recorder provides any desired span of e.m.f. measurement from 0·67 to 100 mV, with a zero shift of up to 50 mV. Figures 1–3 shows the instrumentation. The thermocouples were made from 30-gauge iron–constantan wire, silver-soldered. The furnace was made from a quart Dewar flask surrounded by vermiculite in a large drum. The top of the furnace was sealed with two sheets of asbestos which had holes for the thermocouple leads and the platinum resistance thermometer. A

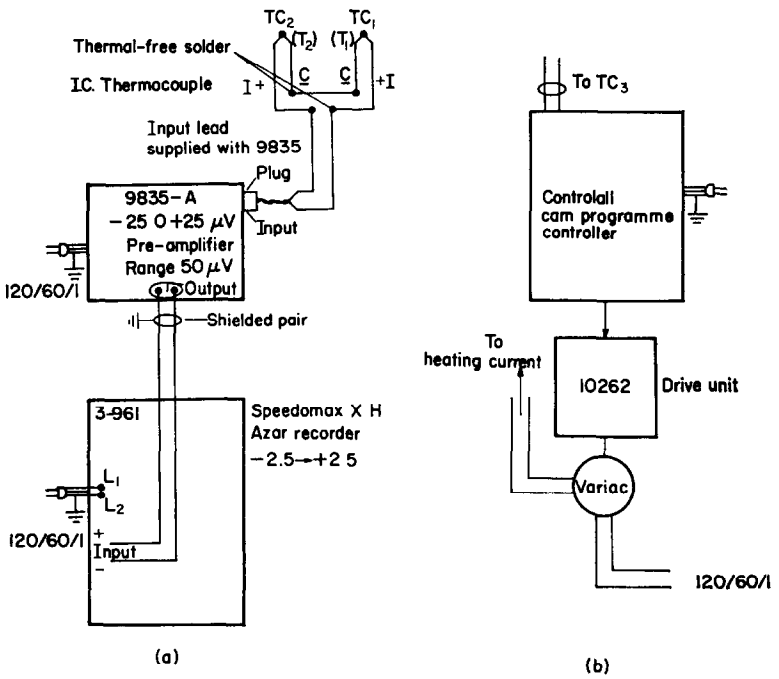


FIG. 1.—(a) Temperature difference measurement.
(b) Controlall and drive unit.

copper cone was used as the reference shield and was placed in a conical heating mantle which served as the heat source. The sample was carefully placed in a test-tube resting on the metal shield, and contained the platinum thermometer and a thermocouple. The other thermocouple was attached to the copper shield.

A controlled constant heating rate in the furnace is essential. Herington used a heating rate of 0·2°/min until the sample was 10° below its melting point.[1] We used a rate of 0·016°/min with an equilibration time of 5 hr. To accomplish this rigorously and check the thermocouple readings, elaborate equipment was used, but not all of it need be used once the system has been standardized. For automatic temperature control, Leeds and Northrup current-adjusting controls were used in conjunction with a saturable-core reactor. These controls supplied *proportional*, *reset*, and *rate* actions for stepless regulation of electric power for precise control of the furnace. A block diagram is given in Fig. 3. The recorder monitored the shield temperature, and deviation from the set temperature was transmitted as an error signal to the current-adjusting control unit which then made an automatic correction. A Leeds and Northrup Controlall assembly (Cat. No. 10171-15) was used for this purpose. Details of its operation can be obtained from the manufacturers, or Friedenberg's work.[4]

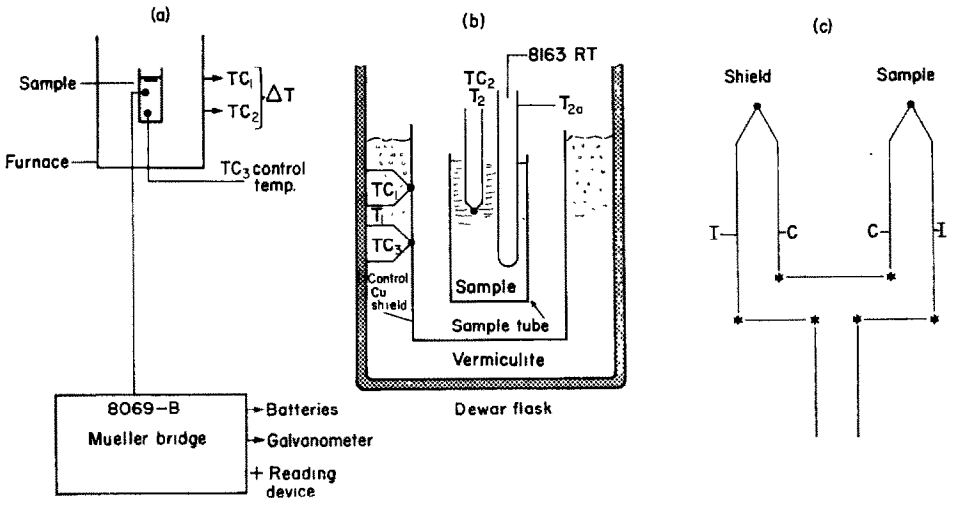


FIG. 2.—(a) Absolute temperature measurement. (b) DTA measurements. (c) Iron–constantan thermocouples for temperature difference measurements. TC_1—thermocouple to shield; TC_2—thermocouple to sample; TC_3—thermocouple to Controlall furnace; 8163 RT_1—platinum resistance thermometer; *L & N thermal-free solder at junctions; I—iron; C—constantan.

The performance of the equipment and of the DTA method was independently checked with a Mueller temperature bridge platinum resistance thermometer (N.B.S. certified) which yielded absolute temperature measurements to a high degree of accuracy.

Procedures

The calculation of impurity concentrations by this DTA method involves three quantities: (*a*) $\Delta(\Delta T_1)$, (*b*) $\Delta(\Delta T_2)$, and (*c*) G. The determination of each will be considered in turn.

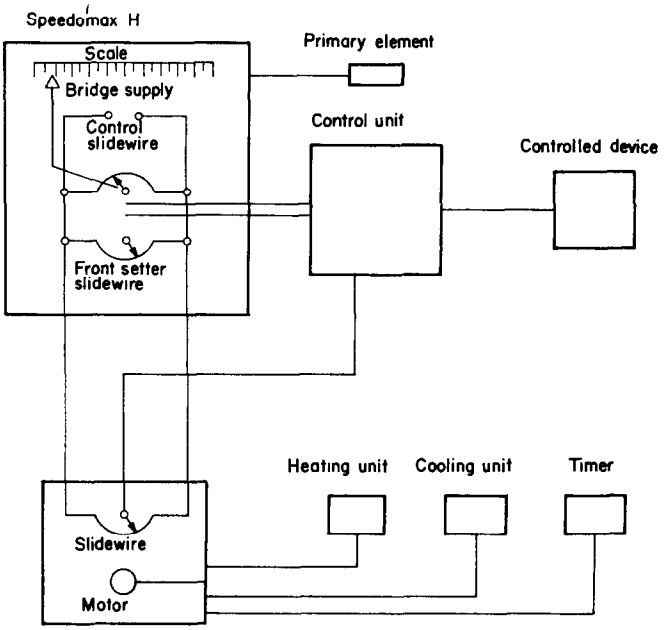
(*a*) Milligram samples are adequate provided the thermocouple junction can be completely immersed in the sample. The recorder automatically plots the temperature difference between sample and shield against time. Although all our experiments were run for 24–48 hr to verify that the slope of the curve was constant, the slope can be measured from any 15- to 30-min section of the premelting heating curve (Fig. 4).

The measurement of differences in temperature is well-known for its sensitivity and accuracy.[5] According to the manufacturers the equipment described here is capable, with some modifications, of measuring temperature differences of 10^{-8} deg. In our experiments the maximum sensitivity of measurement was 10^{-6} deg, but the precision and accuracy were limited by the precision of the chart recorder. Other limiting factors are the heat transfer properties of the system at the point of measurement, and the standardization procedure used to measure the absolute value of the temperature, but these were negligible in comparison.*

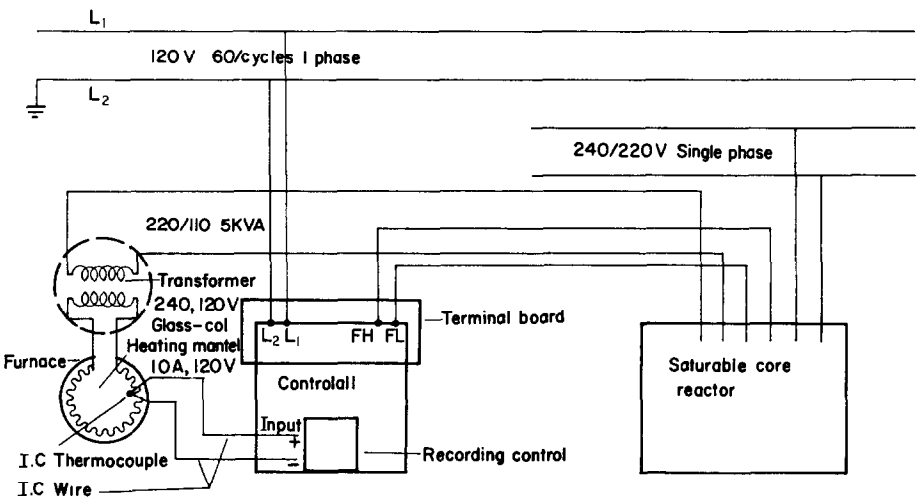
For routine work a sensitivity of 0·01° may be used and three temperature readings suffice to give the slope of the DTA curve. For the ultra-purity determinations reported here a higher sensitivity (0·00001°) was used, and the slope was obtained by the method of least squares from 25–50 readings. Repeating a run under the same conditions always yielded an identical recording. If the rate of heating was increased above 0·05°/min the curves were no longer linear, and this may account for the non-linearity of the curves in Herington's qualitative DTA tracings.

(*b*) The procedure is repeated for the same sample after addition to it of a known quantity of a known substance. The impurity added to naphthalene was benzoic acid. Choice of an impurity to add should be based on the ability of the impurity to form eutectics rather than solid solutions, *e.g.*, benzoic acid rather than β-naphthol. The sample (50 g) is weighed, the impurity is added, and the mixture is melted, mixed well, cooled and reweighed. Weighings should be done as accurately as possible. When 6 successive additions of impurity were made, with a heating run for each, the results gave identical initial concentrations of impurity, so a single addition is sufficient.

* Heat transfer tests were made by Prof. W. H. Hilding, Department of Mechanical Engineering, University of Connecticut.



(a)



(b)

FIG. 3.—(a) Block diagram of Controlall.
(b) Block diagram of apparatus.

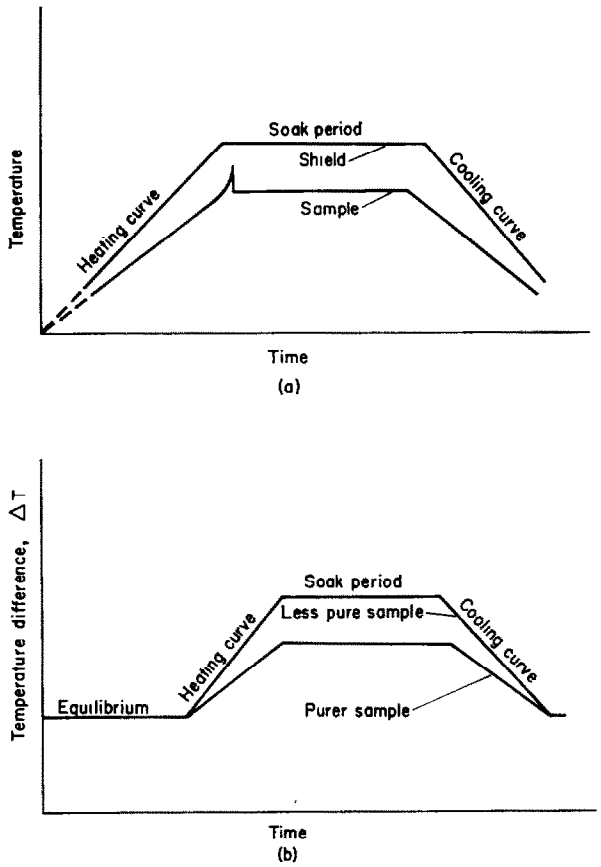


FIG. 4.—(a) Time–temperature curves of shield and sample.
(b) Time–temperature difference curves for two samples of different purity.

(*c*) The proportionality constant G is dependent on external factors associated with the equipment and on the nature of the substance being analysed. The external factors include the heating rate, the characteristics of the shield, the size and insulating properties of the furnace, *etc.* If the instrumentation is not changed, the external factors are constant, and G will then vary for each substance according to equation (10). For the highest accuracy to be achieved, G must be known as accurately as possible, and data from thermal analysis measurements must therefore be used initially to establish the value of G for each substance. This was done with a platinum resistance thermometer (sensitivity 0·00002°) certified by the National Bureau of Standards. Because the readings were taken manually and the conversion of resistance readings into temperature was tedious, a limited number of points was used. As a check, plots were made of sample temperature *vs.* shield temperature. All gave straight lines passing through the origin, as they must if the method is to be valid—see equation (5).

If G is calculated with arbitrary values of K_1 and K_2 it is found to be a singular function for values of K_1 and K_2 that are less than unity (Fig. 5). The experimental values $K_1 = 0{\cdot}99788$ and $K_2 = 0{\cdot}99810$ obtained from thermal analysis measurements would therefore give a singular value for G. Once G has been determined for a given substance any number of samples of any purity can be analysed by this DTA method, rapidly, automatically and accurately.

RESULTS AND DISCUSSION

Table I lists the results of thermal analysis[3] and DTA measurements of the same samples of naphthalene. Each value represents a separate sample, each of which had a minimum of three additions of impurity made to it in the DTA work. The

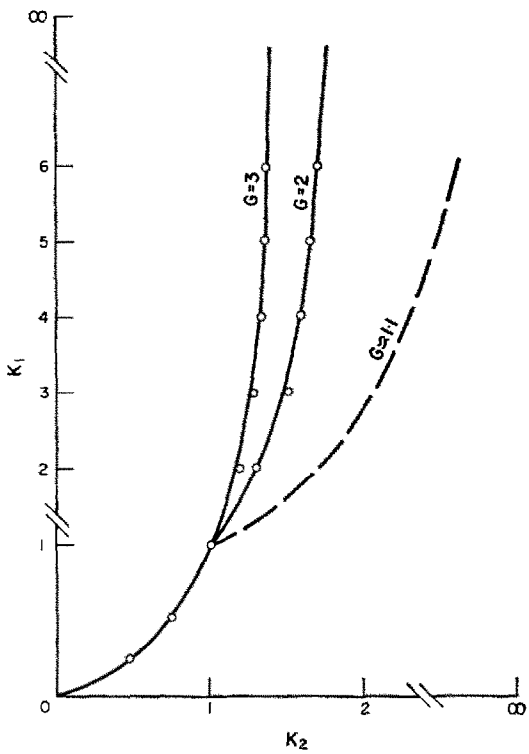


FIG. 5.—Relationship of calibration constant G and slopes K_1 and K_2 [equation (10)].

TABLE I.—DTA AND THERMAL ANALYSIS MEASUREMENTS FOR NAPHTHALENE

Sample	Impurity	
	Thermal analysis *mole%*	DTA *mole%*
Commercial Fisher reagent grade	2·699	2·780
Commercial Baker & Adams reagent grade		1·327
Zone-refined, 1 pass	0·06040	0·06038
	0·06335	0·04557
		0·09581
Zone-refined, 30 passes	$0·00094_7$	$0·00078_8$
	$0·00056_2$	

difference in the results for the commercial samples is explained by the fact that the methods were devised for determination of trace amounts of impurity in ultra-pure materials, and that at higher concentrations the mole fraction of the original impurity plays a dominant role. In the samples purified by zone-refining, the concentration of impurity added to the original sample during the determination is large compared to the original concentration of impurity. The reverse holds for the commercial samples. The results for the zone-refined samples are of a consistent order of magnitude for both methods. The relative error naturally increases as the amount of impurity decreases.

The limiting error is the error in measuring the slope of the differential temperature curves. If a recorder is used the error is likely to be between 1 and 5 parts per 1000. Resistance thermometry does not appear to give much improvement in precision.

This new method provides a rapid automatic technique for purity determinations. Except for mass spectrometry, methods currently available are tedious and lack the necessary sensitivity and accuracy. They have been evaluated elsewhere.[3,4,6] The new method does have some disadvantages, however. Misunderstandings most often arise in distinguishing between the slopes of thermal analysis curves (the rate of change of temperature) and of DTA curves (the rate of change of the difference in temperature between sample and reference). Since the standardization of the method is based on thermal analysis measurements of K_1 and K_2 to give G, and the principles of the two kinds of measurement are quite similar, the disadvantages inherent in cryoscopic methods are apparent here too. The use of mole % as a unit necessitated by measurement of a colligative property is a particular disadvantage. Other methods which yield weight % are more useful but so far lack the necessary accuracy and sensitivity.

The standardization procedure for determining K_1 and K_2 is tedious and is the main disadvantage of the method. For naphthalene K_1 and K_2 are very close to unity and the measurements must be made as accurately as possible, preferably to 5 significant figures; approximations cannot be used. It is possible, however, that other methods of standardization might be used.[4,6,7] The main advantage of standardization by thermal analysis measurements is that G can be evaluated.

The usefulness of these ultra-purity measurements cannot be minimized.[8,9] Numerous theoretical applications to the zone-refining of organic compounds may be verified in practice[7,10] and ultra-purity data obtained for pharmaceuticals.

Zusammenfassung—Ein Verfahren zur raschen quantitativen Bestimmung von Verunreinigungen in ultrareinen organischen Verbindungen wird beschrieben. Es beruht auf dem Unterschied der Steigungen der Kurven, die man erhält, wenn man die Temperaturdifferenz zwischen Probe und einem zum Vergleich dienenden Schild gegen die Zeit aufträgt. Die Ergebnisse werden mit denen der thermischen Analyse verglichen.

Résumé—On décrit une méthode de détermination quantitative rapide des impuretés dans des composés organiques ultra-purs. Elle est basée sur la différence des pentes des courbes obtenues lorsqu'on enregistre la différence de température entre l'échantillon et une référence en fonction du temps. On compare les résultats à ceux obtenus par l'analyse thermique.

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RAPID ANALYSIS OF PLATING BATHS BY A DIRECT-READING THERMOMETRIC METHOD

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Summary—Methods are described for the rapid analysis of plating baths by measurement of the heat evolved in a reaction between the reagent and the component to be determined. The novel feature of the method is the use of reagents which have zero heat of mixing, so that the temperature scale can be directly calibrated in concentration units for a particular determination. A determination takes only 5 min and the precision is equal to that of the classical methods. Procedures are given for the analysis of nickel and chromium plating baths.

PRINCIPLE OF THE METHOD

THE heat change accompanying chemical reactions is proportional to the quantity of reaction products formed. Direct thermometric analysis is based on this principle. An excess of reagent is added to the sample solution; the amount of product formed and the heat change will then be dependent only on the quantity of the component to be determined.

It is difficult to measure the heat of reactions proceeding in solution, but if the experimental conditions are suitably chosen the heat and temperature changes can be made proportional to the amount of component determined.[1–5] The reagent must react selectively with the desired component; with the aid of a calibration curve the temperature change resulting from the reaction can then be translated into a concentration. The calibration curve will not usually pass through the origin, because the heat of reaction will be accompanied by heat from other sources (heat of mixing, dilution, *etc.*) which causes a displacement of the curve.[5–7]

If the calibration curve can be made to pass through the origin, and the influence of the environment can be eliminated, the temperature scale can be calibrated in concentration units, giving the novel method of direct-reading thermometric analysis.

If the calibration curve passes through the origin, the relationship

$$c_m = K\Delta T \tag{1}$$

exists, where c_m is the concentration of the component to be determined (in mole $l.^{-1}$), K is a proportionality constant, and ΔT is the temperature change in °C. The value of K may be calculated from constants characteristic of the system:

$$-QN_m = C\Delta T \tag{2}$$

where Q is the heat of reaction (kcal $mole^{-1}$), N_m is the number of moles of reacting component, and C is the heat capacity of the system (kcal deg^{-1}).

Then

$$c_m = \frac{N_m}{V} = -\frac{C\Delta T}{QV} \tag{3}$$

where V is the volume of the sample solution (in litres), and if C, Q and V are kept constant,

$$K = -\frac{C}{QV} \tag{4}$$

The conditions for this are given below. Any other desired concentration unit may be obtained by means of a conversion factor.

The heat capacity of the system consists of several components:

$$C = C_S + C_R + C_E \tag{5}$$

where C_S, C_R and C_E are the heat capacities of the sample solution, the reagent solution and the apparatus, respectively. If the specific heats of the solutions are known, we can write

$$C_S = V\bar{c}_S\rho_S \tag{6}$$

and

$$C_R = V_R\bar{c}_R\rho_R \tag{7}$$

where $\bar{c}_S$ and $\bar{c}_R$ are the specific heats, V and V_R the volumes, and ρ_S and ρ_R the densities of the sample and reagent solutions respectively. Substituting into equation (3) we have

$$c_m = -\left[\frac{\bar{c}_S\rho_S}{Q} + \frac{V_R\bar{c}_R\rho_R}{QV} + \frac{\bar{c}_E}{QV}\right]\Delta T. \tag{8}$$

From equation (8) it is evident that analytically useful results can only be obtained if all the terms in the bracket are kept constant. This condition is fulfilled if (*a*) the sample solutions and reagent solutions are prepared strictly according to the prescribed procedure, (*b*) the prescribed volumes of solutions are always used, (*c*) the same apparatus or apparatus of the same heat capacity is always used, and (*d*) the reaction chosen always proceeds unequivocally, *i.e.*, the same end products are obtained from the same starting materials.

If these conditions are fulfilled, equation (1) correctly describes the relationship between the concentration of the component to be determined and the temperature change in the solution, provided that no subsidiary reactions occur that are accompanied by temperature changes.

Influence of subsidiary reactions

The subsidiary reactions may be of two kinds—those which cause a temperature change proportional to the amount of the component to be determined, and those which are accompanied by a temperature change independent of the concentration of the component in question.

Subsidiary reactions of the first kind are usually secondary reactions following the chief reaction. The products of the chief reaction react further with some component of the reaction mixture; for instance iron(III) produced in citric acid medium from iron(II) forms a complex with the citrate. The secondary reactions themselves

do not affect the determination if they proceed rapidly and quantitatively, because in this case the relationship between the concentration of the component sought and the temperature change remains linear and only the slope of the calibration curve (*i.e.*, the value of K) varies.

In some subsidiary reactions, however, the heat change (and hence the temperature change) is independent of the concentration of the component to be determined. Such subsidiary reactions occur in the mixing of the sample solution and the reagent solution. For instance, the degree of dissociation or hydration of the dissolved substances changes and the process of mixing is accompanied by cooling or heating according to the direction of the process. In such a case the calibration curve will

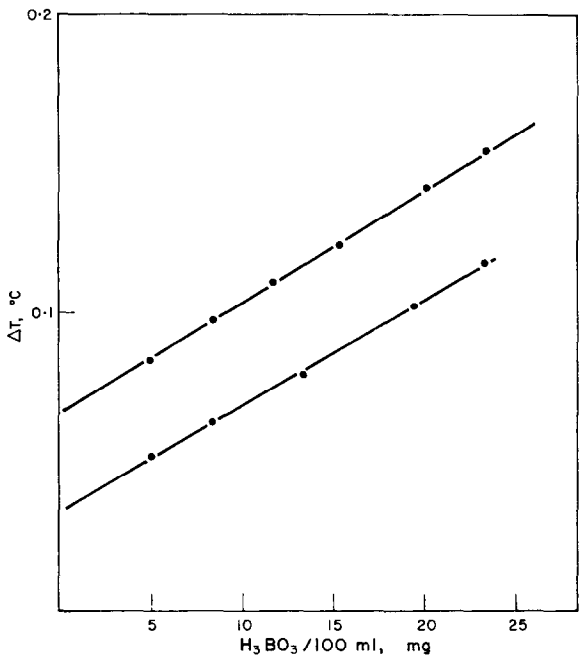

FIG. 1.—Calibration curves for boric acid with addition of 1 or 2 ml of 40% hydrofluoric acid (sample volume 200 ml).

not pass through the origin but will be vertically displaced by a constant amount if the volumes of reagents used are always the same and if the heat of mixing is independent of the concentration of the component sought. In Fig. 1 calibration curves for the boric acid content of nickel baths are shown which have been obtained with various volumes of reagent (1 or 2 ml of 40% hydrofluoric acid). Obviously a small variation of the amount of added reagent causes a sensible change in the heat of dilution and a corresponding displacement of the calibration curve; this is another reason why the reagent should be added in precisely measured quantities. Ideally the heat of mixing is zero; in this case the calibration curve starts from the origin, and it is easy to calibrate the scale of the sensing instrument directly in concentration units.

The prime aim is therefore to obtain a calibration curve starting from the origin. This can be achieved either by adding a non-reacting substance which has a heat of mixing equal and opposite to that of the component causing the side-effect (chemical compensation) or by using a centre-zero scale on the sensing instrument and off-setting the scale to cancel the contribution of the heat of mixing (instrumental compensation). Figure 2 shows the calibration curve for boric acid obtained by adding 2 or 3 ml of hydrofluoric acid with urea added as compensating reagent; the values fall on a single straight line, contrary to Fig. 1.

However, it is more advantageous to use reagents with zero heat of mixing, since the amount of added reagent may then be varied within wider limits, and the same scale zero can be used for each component. The volume of reagent is not critical, because the total volume is very large compared with the reagent volume.

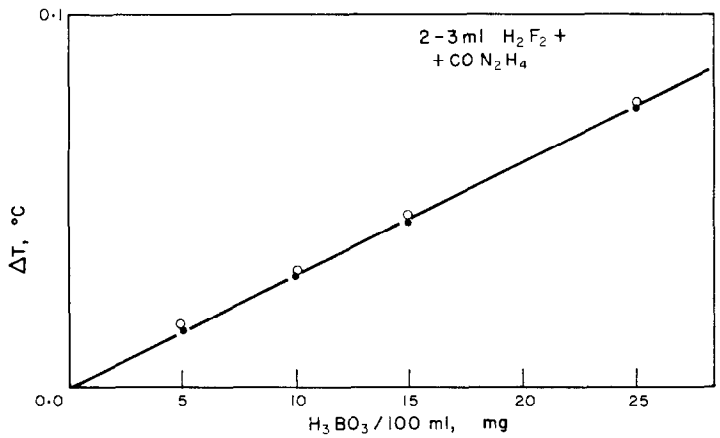

FIG. 2.—Calibration curve for boric acid with addition of 2 or 3 ml of hydrofluoric acid reagent with zero heat of mixing (sample volume 200 ml).

Only two points are really needed on the calibration curve; one of these is the origin. The parameters of the Wheatstone bridge or the shunt of the galvanometer may be adjusted from the analysis of a standard sample of known composition, so that the scale reads directly in the desired concentration units.

Eliminating the influence of the environment

In our calculations so far we have neglected the heat exchange between the system and its environment ($\Delta T'$). This exchange is the resultant of two processes with different rates, namely conduction and evaporation (effects caused by stirring and heat radiation may be neglected). Therefore

$$\Delta T' = t \cdot [\Delta T_1'/\Delta t + \Delta T_2'/\Delta t] \tag{9}$$

where t is the time necessary for the reaction, $\Delta T_1'/\Delta t$ the rate of the temperature change caused by conduction, and $\Delta T_2'/\Delta t$ the rate of the temperature change caused by evaporation.

The value of $\Delta T'$ should be as low as possible. If the temperature of the sample solution is lower than the temperature of the environment the solution will be heated by conduction and cooled by evaporation. At some temperature the rates of heating and cooling must be equal and then the two processes will compensate each other.

It is rather difficult, however, to find this temperature. Therefore in practice the starting temperature is adjusted so as to give only an approximate compensation of $\Delta T_1'/\Delta t$ by $\Delta T_2'/\Delta t$. It is sufficient if the difference in temperature between the sample solution and the environment is adjusted to a few tenths of a degree, which is easily done. We have found that if the temperature of the sample solution is about 0·5° lower than that of the environment the value of $\Delta T'/t$ will lie between 10^{-4} and 10^{-5} deg sec^{-1} which is negligible for fast reactions. The value of $\Delta T'/t$ will of course depend on the composition of the sample solution.

If the temperature of the sample solution is adjusted to make $\Delta T'/t$ negative, the heat transfer to the environment may be compensated by electrically heating the sample solution, and this balances the environmental heat loss for a relatively lengthy period (1–2 min). In this way a quasi-isothermal, quasi-adiabatic system can be established.

Because the temperature coefficients of the two heat-exchange processes will not be the same, the change in temperature of the solution caused by the reaction should affect $\Delta T'/t$, but in practice the effect is negligible because the calibration curve obtained under the same conditions provides an automatic compensation.

The heat exchange with the environment may, then, be neglected in practice, especially if the reaction time is short. The reaction should therefore proceed as rapidly as possible, and in precipitation reactions crystal seeds are often added to the solution to increase the rate of precipitation (*e.g.*, determination of sulphur).

PRACTICAL METHODS OF DETERMINATION

In direct-reading thermometry the same amount of reagent is always added to the sample solution in one batch, and there must be a surplus of reagent even if the component to be determined is present in the highest possible concentration. The surplus permits the use of reactions which are still incomplete at the equivalence point (*e.g.*, formation of complexes of low stability or of precipitates with high solubility) since it displaces the equilibrium in the required direction. Sluggish reactions can also be used because the heat transfer to the environment is negligible for periods of 1–2 min.[5–8]

It is very important to have all solutions at the same temperature before mixing them, especially if the expected temperature change is small or if the volume of the reagent solution is much larger than the volume of the sample solution; in such cases the results may be rather dubious if the temperature difference between the two solutions is a few hundredths of a degree. This is best done by having both reagents in the same vessel, but separated from each other. When their temperatures are the same they can be mixed. A thermostat is not needed, because the sample solution acts as thermostat for the reagent solution (see Fig. 3). This apparatus is very simple and suitable for plant determinations.[6,8]

If a concentrated reagent solution is used, its volume is small compared to the volume of the sample solution, and the solutions come to thermal equilibrium within 2–3 min even if the original temperature difference is as high as 3°.[6] Large sample

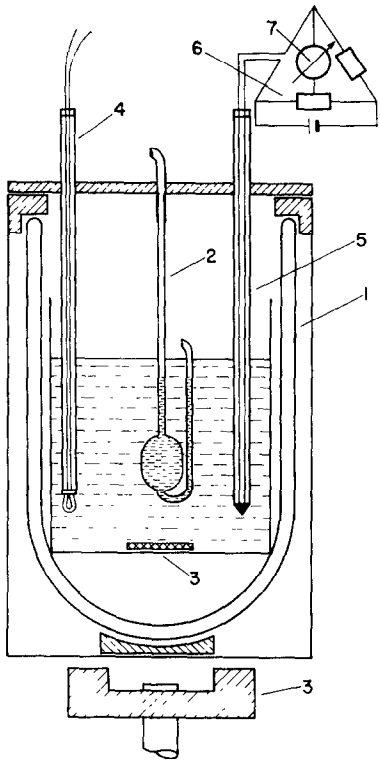

FIG. 3.—Schematic drawing of the apparatus: 1—Dewar vessel; 2—submersible pipette; 3—magnetic stirrer; 4—heater; 5—thermistor; 6—Wheatstone bridge; 7—galvanometer.

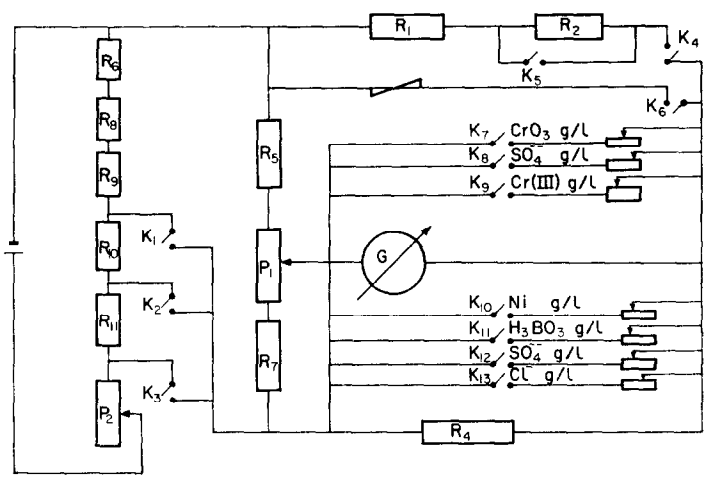

FIG. 4.—Schematic circuit diagram of the Wheatstone bridge.

volumes should be used to give a high heat inertia and low sensitivity to temperature variations in the environment.[6]

EXPERIMENTAL

Apparatus

The apparatus is shown in Fig. 3 and consists of a Dewar vessel, a submersible pipette,[8] a stirrer, a heater, a thermistor, a Wheatstone bridge and a galvanometer or digital voltmeter. The schematic circuit diagram of the Wheatstone bridge is shown in Fig. 4. A moving scale galvanometer with a sensitivity of 10^{-9}A and a scale divided into 1000 parts, or a digital voltmeter with a sensitivity of 10 mA was used as the reading instrument.[9] Suitable resistances can be used in conjunction with the galvanometer or digital voltmeter to give a scale calibrated in the desired concentration units.

Procedure

Transfer by pipette the prescribed amount of the plating bath sample into a 200-ml standard flask, add the reagents necessary for the particular determination, and dilute to the mark with distilled water. Adjust the temperature of the sample solution to 0·5° below the temperature of the environment. Put the sample solution in the Dewar flask. Fill the submersible pipette to the mark with the reagent (with zero heat of mixing). Rinse off the reagent surplus from the outside of the pipette and introduce the pipette into the sample solution (the reagent may also be introduced in a platinum crucible instead of in the pipette). Put the heater, thermistor and stirrer into the sample solution. Switch on the stirrer and allow a pause of 2 min for equilibration.

Then switch the measuring bridge to the most sensitive stage (0·2°/1000 scale divisions) and compensate with potentiometer P1 to bring the galvanometer pointer to about 100 scale divisions; observe the heat exchange between the sample solution and the environment for about 30 sec. If the starting temperature of the sample solution has been correctly adjusted the temperature of the solution will fall by about 0–30 scale divisions in 30 sec. Compensate the cooling of the solution by switching on the heater and adjusting its resistance until the temperature of the sample solution remains practically constant for periods of about a minute.

Introduce the shunt for direct reading of the concentration in g/l, and compensate the bridge by potentiometer P1 to bring the galvanometer pointer to zero on the scale. Transfer the reagent from the submersible pipette into the sample solution with the aid of a rubber bulb. At the end of the reaction, which is shown by the instrument pointer stopping, read off the concentration of the component sought.

The necessary resistance values of the shunts are obtained by use of model solutions which contain known concentrations of the components to be determined. The shunt should be chosen so that the scale is fully utilized, *e.g.*, for an expected content of 10–100 g/l the full scale deflection should correspond to 100 g/l. The shunt resistance values may be adjusted easily if continuously variable resistances are used as shunts. A model solution of known composition is used and the shunt is varied until the scale reading gives directly the concentration of the component present in the model solution. All the usual types of analytical reaction can be used.[10]

RAPID ANALYSIS OF NICKEL BATHS

Nickel

Reagents

Sodium tartrate solution. Dissolve 1 kg of tartaric acid in distilled water, dilute to 2 l. and add 3 l. of 30% sodium hydroxide solution.

Model nickel bath. This contains 400 g of nickel sulphate heptahydrate, 30 g of boric acid and 30 g of sodium chloride per l.

Potassium cyanide solution with zero heat of mixing. Dissolve 500 g of potassium cyanide in 100 ml of water and 100 ml of 30% sodium hydroxide solution. Add 515 ml of glycerine to the solution. *Control of the reagent:* dilute 50 ml of the sodium tartrate solution to the mark in a 200-ml standard flask. Transfer the solution to the apparatus and add 8 ml of the potassium cyanide solution. If the solution cools or gets warmer, adjust the cyanide solution by addition of a few ml of glycerine or a few g of potassium cyanide and test again. Repeat the adjustment until the heat of mixing practically disappears.

Method

Take 2 ml of the nickel sample in a 200-ml standard flask and add 50 ml of distilled water and—with vigorous stirring—50 ml of sodium tartrate solution. Dilute to the mark with distilled water,

and analyse the solution with 8 ml of the potassium cyanide solution as reagent. The results of the analysis of baths with various nickel contents are shown in Table I.

TABLE I.

Number	Nickel content: EDTA titration g/l	Thermometric method g/l	Difference g/l
1	94·3	94·7	+0·4
2	83·0	81·7	−1·3
3	64·0	64·6	+0·6
4	52·7	52·8	+0·1
5	48·0	47·2	−0·8
6	37·6	37·4	−0·2
7	10·1	10·2	+0·1

Boric Acid

Reagents

Hydrochloric acid (s.g. 1·12).

Sulphuric acid (s.g. 1·6).

Hydrofluoric acid with zero heat of mixing. Dissolve 34 g of carbamide in 205 ml of 40% hydrofluoric acid. *Control of the reagent:* dilute 20 ml of hydrochloric acid (s.g. 1·12) and 50 ml of sulphuric acid (s.g. 1·6) to the mark in a 200-ml standard flask with distilled water. Transfer the mixture to the apparatus and add 5 ml of the hydrofluoric acid reagent from a platinum crucible. If the sample solution cools or gets warmer, add hydrofluoric acid or carbamide to the reagent until on repetition of the control the heat of mixing practically disappears.

Method

Take 20 ml of the nickel bath in a 200-ml standard flask, add 20 ml of hydrochloric acid (s.g. 1·12) and 50 ml of sulphuric acid (s.g. 1·6), dilute to the mark with distilled water and transfer to the apparatus. Add 5 ml of the hydrofluoric acid reagent from a platinum crucible. Table II shows typical results.

TABLE II.

Number	Boric acid content: Added g/l	Thermometric method g/l	Difference g/l
1	10·0	10·3	+0·3
2	17·0	17·5	+0·5
3	23·0	23·3	+0·3
4	30·0	30·0	0·0
5	33·0	33·6	+0·6
6	41·0	41·1	+0·1
7	45·2	45·0	−0·2

Sulphate

Reagents

Hydrochloric acid (s.g. 1·12).

Barium sulphate suspension. Suspend 100 g of barium sulphate in 400 ml of distilled water.

Precipitating reagent with zero heat of mixing. Dissolve 39·5 g of barium chloride in 155 ml of distilled water and add 30·5 ml of hydrochloric acid (s.g. 1·12) to the solution. *Control of the reagent:* take 20 ml of hydrochloric acid (s.g. 1·12) in a 200-ml standard flask, add 5 ml of barium sulphate suspension and dilute to the mark with distilled water. Transfer the solution to the apparatus and add 10 ml of precipitating reagent. If the solution cools or gets warmer, add a few ml of hydrochloric acid or a few g of barium chloride until on repetition of the control the heat of mixing practically disappears.

Method

Take 5 ml of the bath in a 200-ml standard flask, add 20 ml of hydrochloric acid (s.g. 1·12) and 5 ml of barium sulphate suspension, and dilute to the mark with distilled water. Analyse with 10 ml of the precipitating reagent. Typical results are shown in Table III.

TABLE III.

Number	Sulphate content: Gravimetric method *g/l*	Thermometric method *g/l*	Difference *g/l*
1	71·3	73·0	+1·7
2	91·5	92·0	+0·5
3	164·7	165·0	+0·2
4	109·8	109·0	−0·8
5	126·1	124·0	−2·1
6	146·4	145·0	−1·4

Chloride

Reagents

Nitric acid (s.g. 1·2).

Precipitating reagent with zero heat of mixing. Dissolve 240 g of silver nitrate in 400 ml of water; add 96 ml of 96% ethanol and 50 ml of nitric acid (s.g. 1·2) to 380 ml of the solution. *Control of the reagent:* dilute 15 ml of nitric acid (s.g. 1·2) to the mark in a 200-ml standard flask with distilled water. According to the general working procedure add 5 ml of reagent. If the sample solution gets warmer or cooler, adjust the reagent with a few g of silver nitrate or a few ml of alcohol.

Method

Take 20 ml of the plating bath in a 200-ml standard flask, add 15 ml of nitric acid (s.g. 1·2) and dilute to the mark. Then add 5 ml of silver nitrate solution as reagent according to the general working procedure. Some results are shown in Table IV.

TABLE IV.

Number	Chloride content: Gravimetric method *g/l*	Thermometric method *g/l*	Difference *g/l*
1	1·98	2·0	+0·02
2	5·26	5·2	−0·06
3	9·92	9·9	−0·02
4	16·50	16·4	−0·10
5	18·2	18·2	0·00
6	23·0	23·1	+0·10

RAPID ANALYSIS OF CHROMIUM BATHS

Chromic Acid

Reagents

Sulphuric acid (s.g. 1·6).

Model chromium bath. This contains 400 g of chromic acid, 10 g of chromium(III) chloride and 20 g of sulphuric acid per l.

Iron(II) sulphate solution with zero heat of mixing. Dissolve 200 g of iron(II) sulphateheptahydrate in 440 ml of distilled water. Add 150 ml of sulphuric acid (s.g. 1·6) to the solution. *Control of the reagent:* dilute 50 ml of sulphuric acid (s.g. 1·6) to 200 ml with distilled water and add 5 ml of iron(II) sulphate solution according to the general working procedure. If the sample solution cools or gets warmer, adjust the reagent with a few ml of sulphuric acid or a few g of iron(II) sulphate heptahydrate.

Method

Transfer 10 ml of the chromium bath to a 100-ml standard flask and dilute to the mark with distilled water. Transfer 5 ml of the diluted solution to a 200-ml standard flask, add 50 ml of sulphuric acid (s.g. 1·6) and dilute to the mark with water. According to the general working procedure add 5 ml of iron(II) sulphate reagent. The results obtained for the chromic acid contents of various chromium baths are shown in Table V.

TABLE V.

Number	Chromic acid content: Volumetric method *g/l*	Chromic acid content: Thermometric method *g/l*	Difference *g/l*
1	435·2	434·0	−1·2
2	397·4	399·0	+1·6
3	321·3	321·0	−0·3
4	169·2	168·0	−1·2
5	157·3	158·0	+0·7
6	158·1	158·0	−0·1

Chromium(III)

Reagents

Sodium hydroxide, 30% solution.

Potassium permanganate solution with zero heat of mixing. Add 30 ml of 28% sodium chloride solution and 0·2 ml of 30% sodium hydroxide solution to 70 ml of cold saturated potassium permanganate solution. *Control of the reagent:* dilute 30 ml of 30% sodium hydroxide solution to 200 ml with distilled water. According to the general working procedure add 5 ml of reagent. If the solution gets warmer or cooler, adjust the reagent with a few ml of sodium chloride or potassium permanganate solution.

Method

Transfer 10 ml of the chromium bath to a 200-ml standard flask, add 30 ml of 30% sodium hydroxide solution and dilute to the mark with distilled water. According to the general working procedure add 5 ml of potassium permanganate reagent. Table VI shows typical results.

TABLE VI.

Number	Chromium(III) content: Volumetric method *g/l*	Chromium(III) content: Thermometric method *g/l*	Difference *g/l*
1	3·92	3·98	+0·06
2	3·63	3·71	+0·08
3	2·94	2·90	−0·04
4	1·72	1·67	−0·05
5	1·35	1·40	+0·05
6	0·67	0·68	+0·01

Sulphate

The sulphate content of chromium baths is determined on the same principle as described in the determination of the sulphate content of nickel baths. It must be remembered, however, that the results obtained for the sulphate content show a negative error dependent on the chromic acid content and therefore the results must be corrected for the chromic acid content.

Since the sulphate content of chromium baths is much lower than that of nickel baths the determination must be performed with larger samples and the value of the shunt calibrated for sulphate content is adjusted with a sulphuric acid solution of known concentration so as to obtain the sulphate content of the solution directly in g/l even for these larger samples.

Method

Take a 20-ml sample of the chromium bath and perform the analysis according to the procedure for determining the sulphate content of nickel baths. Correct the results according to the chromium content of the bath. For every g of chromic acid present per litre, increase the determined sulphate content by 0·05 g/l.

Some results obtained in the analysis of chromium baths with different sulphate contents are shown in Table VII.

TABLE VII.

Number	Sulphate content: Gravimetric method *g/l*	Thermometric method *g/l*	Difference *g/l*
1	87·2	86·0	−1·2
2	62·8	64·0	+1·2
3	38·1	36·0	−2·1
4	27·4	28·0	+0·6
5	13·2	14·0	+0·8
6	9·6	9·0	−0·6

Zusammenfassung—Methoden zur Schnellanalyse von Plattierungsbädern werden beschrieben, bei denen die in einer Reaktion zwischen Reagens und zu bestimmender Verbindung entwickelte Wärme gemessen wird. Neu ist an der Methode, daß Reagentien ohne Mischungswärme verwendet werden, so daß die Temperaturskala für eine besondere Bestimmung direkt in Konzentrationseinheiten geeicht werden kann. Eine Bestimmung dauert nur fünf Minuten und die Genauigkeit ist dieselbe wie bei den klassischen Methoden. Vorschriften zur Analyse von Vernickelungs und Verchromungsbädern werden angegeben.

Résumé—On décrit des méthodes pour l'analyse rapide des bains de galvanoplastie par mesure de la chaleur dégagée dans une réaction entre le rèactif et le composant à déterminer. Le nouveau caractère de la méthode réside dans l'emploi de réactifs dont la chaleur de mélange est nulle, de sorte que l'échelle de température peut être directement étalonnée en unités de concentration pour une détermination particulière. Une détermination ne nécessite que 5 mn et la précision est égale à celle des méthodes classiques. On donne des techniques d'analyse de bains de nickelage et chromage.

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IMPROVED METHOD FOR THE CONSTANT-CURRENT POTENTIOMETRIC DETERMINATION OF PLUTONIUM

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Summary—A highly precise method is described for the determination of plutonium by constant-current potentiometric titration with primary standard potassium dichromate. The relative standard deviation is 0·04% or better.

THE precise constant-current potentiometric titration of plutonium with National Bureau of Standards primary standard potassium dichromate as titrant[1] has been used successfully for several years at this laboratory. In order to obtain acceptable precision (relative standard deviation <0·1%) with 100 mg samples, a weight burette was used to titrate 99% of the plutonium content, and a microburette was used to complete the determination. With the increasing availability of plutonium, larger samples can now be used to minimize the weighing and titration errors. Accordingly, the potentiometric titration has been modified so that 250–450 mg of plutonium are determined by a direct weight titration with a more concentrated titrant, to give results with a relative standard deviation of about 0·04% or better. The method may be used for the titration of smaller samples, with somewhat less precision (~0·10%).

EXPERIMENTAL

Apparatus

Weight burette. A 30-ml Friedman–LaMer-type burette with Teflon stop-cock is used. The tip of the burette is drawn out to a fine opening and silicone-treated.

Titration apparatus. This equipment has been described previously.[1] The gold electrodes (35 × 5 × 1 mm) are cut from polished gold sheet and gold-soldered to platinum rods (1–2 mm diameter). The gold electrodes are immersed to a depth of about 15 mm in the solution to be titrated. No special care or pretreatment of these electrodes is required except for occasional wiping with acetone to remove any surface organic films.

Reagents

Sulphuric acid, 1*N*, reagent grade.

Potassium dichromate solution, 3 mg of potassium dichromate per g of solution.[1]

Procedure

Dissolve the plutonium metal or compound by standard methods.[2] If organic material, *e.g.*, from ion-exchange or solvent extraction procedures, is suspected to be present, it must be removed by fuming with a nitric–sulphuric acid mixture to which a small amount of perchloric acid (<0·5 ml) has been added. Solutions containing chloride, fluoride, nitrate or perchlorate must be heated to incipient dryness with sulphuric acid several times. Dissolve the residue in a minimum amount of 1*N* sulphuric acid and cool.

Pour the plutonium(IV) solution into the Jones reductor. Using air pressure from a rubber bulb at the top of the reductor, force the plutonium solution through the reductor at a flow-rate of about 20–30 ml/min. Rinse the sample beaker several times with 1*N* sulphuric acid, adding the washings to the reductor. Wash the reductor at least twice with 15-ml portions of 1*N* sulphuric acid. Collect the reduced plutonium(III) in a 150-ml beaker containing a Teflon-coated magnetic stirring bar.

Complete the reduction step in about 5 min to avoid possible air-oxidation of plutonium(III). Collect up to 75 ml of solution for titration.

Rapidly set up the titration apparatus and adjust the magnetic stirrer so that it agitates without spattering or introducing air into the solution. Add the titrant from a weight burette containing about 30 ml of the dichromate solution, until the blue colour of the sample just changes to pale green-brown.

Adjust the pH meter to read 700 mV and quickly add the titrant in 5-drop portions until the potential of the system reverses. Continue the titration until the potential has changed by 10 mV and then add the titrant dropwise until the first potential change of greater than 10 mV occurs. Weigh the burette and continue the titration, recording the change in potential and weighing each increment (about 10 mg) of titrant added. Continue the titration past the end-point until the addition of one drop of titrant changes the potential by 10 mV or less. The end-point is obtained in the usual way by a derivative plot or is accurately calculated by Yan's method[8] as modified for weight titrations. The end-point break usually starts at 580–680 mV.

RESULTS

National Bureau of Standards plutonium metal sample No. 949 and the proposed primary standard compounds, plutonium sulphate tetrahydrate,[4] anhydrous plutonium sulphate[5] and dicaesium plutonium hexachloride,[6] were used for evaluation of the method. Table I shows that acceptable results are obtained with these materials.

TABLE I.—DETERMINATION OF PLUTONIUM BY CONSTANT-CURRENT POTENTIOMETRY WITH NBS POTASSIUM DICHROMATE

Sample	Weight taken, *g*	Plutonium given, %	Plutonium found, %**	Relative standard deviation, %
Pu metal (NBS949)	0·3	99·93*†	99·93	0·02
$Pu(SO_4)_2 \cdot 4H_2O$	0·9	47·51‡	47·53	0·04
$Pu(SO_4)_2$	0·7	55·45‡	55·44	0·02
Cs_2PuCl_6	1·0	33·33†¶	33·32	0·03

* Certified value, corrected for ^{241}Am growth.
† Relative standard deviation 0·03%.
‡ Theoretical value.
¶ Analysed value, Dow Chemical Co.
** Mean of 4 results.

Determination of plutonium in over 50 samples of plutonium sulphate tetrahydrate, made at intervals during several years, has indicated a relative standard deviation of 0·04% for the method.

DISCUSSION

The fine tip of the burette allows delivery of the titrant in drops weighing 10–30 mg. The drops from the silicone-treated tip are relatively reproducible in size and are easily dispensed. Weight increments of about 10 mg of titrant (equivalent to about 0·15 mg of plutonium) will usually provide a potential change of at least 100 mV at the end-point. Larger increments up to about 30 mg provide potential changes greater than 400 mV.

Meter readings for potential changes of 10 mV or less are stable almost immediately after dropwise addition of titrant, but near the end-point may require about 10 sec to reach a stable value. The potential change at the end-point, 100–400 mV, may take as long as 3 min for completion. Stable potential readings are indicated by a drift of less than 10 mV in 10 sec.

The final titration in the earlier method[1] required 4*N* sulphuric acid for a sharp end-point, probably because of the very small increments of dichromate (0·01 mg) added. The present method uses from 3 to 9 times as much dichromate in each increment added near the end-point and apparently requires only 1*N* sulphuric acid for a satisfactory end-point. The use of 1*N* sulphuric acid reduces the amount of "gassing" in the Jones reductor and makes the reduction step faster, especially when large plutonium samples are used.

The tip of the burette need not be capped at any time. The silicone treatment prevents titrant from adhering to the outside of the tip during the titration, and prevents loss by evaporation. There is less than a 2-mg change in the weight of the loaded burette during 24 hr.

Cations such as those of Cr, Fe, Mo, Ti, U, V and W which are reduced in a Jones reductor, interfere, but repeated analysis of the same plutonium material by this method over a period of several years has indicated no significant interference from americium as has been suspected in ceric sulphate titrations.[6] A correction for these interfering cations may be applied, or better, they may be removed by anion-exchange methods.[7] It must be realized that applying corrections for certain elements such as uranium and chromium which are reduced in a Jones reductor to a mixture of oxidation states, *e.g.*, U(III)-U(IV), Cr(II)–Cr(III), may introduce significant errors in the plutonium value if the concentration of the interfering element is high enough. When nitric acid anion-exchange procedures are used to remove impurities, organic material (apparently leached from the resin) causes positive errors if it is not destroyed before the titration. The errors have been found to be consistent for particular brands (or grades) of anion-exchange resin.[8] Results high by 0·28 % were obtained with one brand of standard Dowex-1 resin, but the results were high by only 0·05% when AG-1 resin[9] (a specially purified, treated and graded form of Dowex-1) was used. This interference can be reduced or entirely eliminated by fuming the samples with a nitric–sulphuric–perchloric acid mixture. Treatment with nitric or sulphuric acid, alone or mixed, did not remove the organic matter even after repeated fumings.

Résumé—On décrit une méthode hautement précise de dosage du plutonium par titrage potentiométrique à intensité constante avec pour étalon primaire le bichromate de potassium. L'écart type relatif est de 0,04%, ou meilleur.

Zusammenfassung—Es wird eine sehr genaue Methode zur Bestimmung von Plutonium durch potentiometrische Titration bei konstantem Strom mit dem primären Standard Kaliumdichromat beschrieben. Die relative Standardabweichung ist 0,04% oder besser.

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AN EXPERIMENTAL EVALUATION OF NEUTRON ACTIVATION, WET ASSAY AND FIRE ASSAY METHODS OF DETERMINING GOLD IN ORES

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Summary—The errors associated with fire assay, wet extraction and neutron activation methods are evaluated, the accuracy and precision of these methods are compared, and a method of determining chemical recovery in the activation determination of gold in ores and concentrates is presented.

THE gold content of ores has been estimated by fire assay and cupellation since at least the 16th century. Recently, wet methods of extracting gold have been recorded and neutron activation has been developed into a potentially useful method of determination. However, very little has been recorded to permit an evaluation of the various methods for determining gold in ores, or to allow assessment of the efficiency of fire assay and wet extraction for the separation and collection of microgram amounts of gold. The purpose of the present research was to remedy this situation.

EXPERIMENTAL

Apparatus

William and Wilson 20 kW electric furnace.
Beckman Model B spectrophotometer.
Sartorius MPR 5/2 microbalance.
Nuclear Chicago Model 410A single channel spectrometer and Model 422 well-type scintillation detector.
Cupels and assay crucibles supplied by A. P. Green Fire Brick Co. (Weston, Ontario, Canada).

Reagents

Gold foil (Johnson Matthey).
Gold, precipitated powder (Fisher purified).
Silver, precipitated powder (Fisher certified reagent).
Lead foil (Matheson, Coleman and Bell reagent).
All acids and other chemicals used were commercially pure reagent grade except the hydrobromic acid which was the colourless fraction obtained by distillation of reagent grade acid.

Standard gold solutions

Approximately 1 g of gold foil was dissolved in *aqua regia* and nitrous oxides were removed by repeated evaporations with hydrochloric acid in the presence of a few milligrams of sodium chloride. The solution was filtered and the residue ignited, dissolved by the same procedure and added to the original filtrate. The final solution was diluted to 1 l. with 0·12*M* hydrochloric acid. Dilute gold solutions were prepared by dilution with 0·12*M* hydrochloric acid. The concentrated stock solution was standardized with hydroquinone.[1]

Standard methods used for determining gold

Gravimetric. After annealing at 700° for a few minutes, the gold residue was transferred directly to the balance pan by tweezers or by careful brushing. Alternatively, the residue was collected by filtration, the filter paper and contents were placed in a tared crucible and the sample heated to constant weight at 700°. A blank was necessary to correct for the filter ash. With some samples, the gold was dissolved in *aqua regia* and then precipitated from the solution and determined by hydroquinone.[1]

Titrimetric. The iodometric technique[8] was used to determine 0·2–25 mg of gold.

Spectrophotometric. The direct bromoaurate procedure[2] is one of the simplest colorimetric methods available for gold and was used to determine 10–500 μg of gold which had been isolated from interfering elements. The bromoaurate was formed in 0·8M hydrobromic acid and the absorbance measured at 380 mμ.

For amounts of gold from 1–10 μg, the Methyl Violet procedure[3] was applied. The absorbance of the coloured species was measured at 600 mμ.

THE FIRE ASSAY

The long use of the fire assay has encouraged the belief that it is precise and accurate under all circumstances. This assumption has been supported by the authors of a few reports who proposed to determine the accuracy of the fire assay, but provided only a comparison of the efficiency of different assay procedures and perhaps of the various assayers. Despite the lack of experimental justification for the use of the classical assay and the uncertainty of the chemistry of the interactions of the flux constituents, the technique is the most universally used method for the estimation of gold in ores.

We have tried to obtain a realistic appraisal of the fire assay procedures for both milligram and microgram amounts of gold.

The fire assay of standard gold samples

Both the normal and the nitre assay methods were evaluated by using standard gold samples. The fluxes used were A and B respectively (Table I).

Each set of samples was prepared from a mixture of the flux with the appropriate amount of a blank ore. For the normal assay, the blank ore was pure silica, and for the nitre assay, it consisted of a mixture of silica and iron, copper and nickel sulphides. After thorough mixing of the blank ore with the flux, samples were weighed and transferred to an assay crucible, and salted individually with a known amount of gold. Some samples were salted with milligram amounts of pure gold powder and then thoroughly mixed on a cellophane sheet. Others were salted with either milligram or microgram amounts of gold added as a standard solution of gold chloride. These samples were dried overnight at 85°, cooled, stirred gently to break up any large lumps, and then mixed.

The crucibles containing the samples were placed in the furnace at 1040° and heated to 1150° as quickly as possible (usually 45–60 min). After 30 min at 1150°, the crucibles were removed and the samples poured into a conical iron mould in which they were allowed to cool. The slag could be separated from the lead button by gentle tapping with a small hammer.

The lead buttons were cupelled, the silver beads parted, and the gold was determined either by direct weighing of the gold residue or by the bromoaurate colorimetric method, depending on the amount of gold added to the assay sample. In all cases, blank corrections were applied.

The values for the normal fire assay show that an average of 99% or more of the gold was recovered for milligram amounts and 97% or more for microgram amounts of gold added. Equally complete recovery was obtained from samples salted with gold powder or with a gold solution. Similar recovery of gold was obtained with the nitre assay.

Although the values show excellent precision and accuracy, it was found that precise results can be expected for ore samples only if the gold can be rendered as readily amenable to collection as with the standard samples. This is sometimes extremely difficult to achieve, but with many ores a proper choice of flux can be made.

The cupellation and parting of gold standards

The cupellation and parting methods were evaluated by using artificial lead buttons (~23 g in weight) containing gold and silver. Weighed amounts of the pure metal powders were placed in a lead foil boat and the boat folded carefully to avoid loss during handling. Other artificial buttons were prepared by evaporation (at 85°) of an aliquot of gold chloride solution in a boat made of lead foil. The volume and the acidity of the solution were kept to a minimum to limit the corrosion of the lead and prevent possible losses of solution. After the addition of silver powder, the lead was folded into a $\frac{3}{4}$ in. cube.

Magnesia cupels were preheated in the furnace to 982° and the lead buttons were added quickly to prevent "freezing." After "opening" for 5 min at this temperature, the draught was opened and the sample "driven" for 25–30 min. The draught was then closed, and after a "finishing" time of 5 min the cupels were withdrawn from the furnace gradually, to prevent "splitting".

Two parting procedures were used. For milligram amounts of gold, the bead was parted with

TABLE I.—FLUX COMPOSITIONS

	Gold ores	Nickel ores			Cupel assay
	A, *g*	B, *g*	C, *g*	D, *g*	E, *g*
Ore*	15	30	15	30	40‡
PbO	85·0	275	250	266	37·5
SiO_2	(10)†	15	10	60	—
Na_2CO_3	21·1	40	12	46	22·5
CaO	4·5	12	—	12	—
$Na_2B_4O_7$	—	—	—	—	37·5
KNO_3	—	16	9	18	—
Flour	1–3	—	—	—	2

* For blanks, 15 g of silica replaced 15 g of gold ore and a mixture of 12 g of silica, 3 g of copper sulphide, 3 g of nickel sulphide and 12 g of iron sulphide replaced 30 g of nickel ore.
† Ten g of silica were added to the flux for gold ores No. 295 and No. 305.
‡ The cupel material contained lead oxide from the cupellation.

5–10 ml of hot 5*M* nitric acid in a glazed porcelain crucible. The solution was decanted and the residue washed thoroughly. After annealing, the gold was weighed directly. For milligram and microgram amounts of gold, the bead was parted in a small beaker and the residue filtered off on a 7-cm Whatman No. 42 filter paper. For milligram amounts, the filter was placed in a tared crucible, charred, and heated at 700° to constant weight. With microgram amounts, the filter was returned to the parting beaker and the paper removed by heating at 450° for several hr. After cooling, the gold was dissolved and then determined by the bromoaurate method. Blanks were done with all procedures. Occasionally silver chloride formed because of hydrochloric acid fumes, and the samples were then washed with aqueous ammonia (1 + 1) and then with water.

The losses resulting from the decantation procedure depended on the skill of the operator. With coherent residues, losses were minimal but with scattered residues the probability of losses was greatly increased. Losses of gold by dissolution in the nitric acid or by passage of very fine particles through the filter were evaluated by fire assay of the evaporated filtrate, using flux A with 15 g of silica. The maximum amount of gold found in the filtrate was 0·3% of the gold added.

The recovery of gold from artificial buttons containing milligram amounts of gold powder was usually 99·5% or better. Losses during decantation cause low values and incomplete parting causes high values. Varying proportions of gold and silver do not affect the recovery. Samples which were parted a second time showed no significant loss in weight.

For buttons containing gold added as a solution the recovery was greater than 97% for microgram amounts but only 90–95% for milligrams amounts of gold. When the gold chloride solution was added to the lead boats, gold was precipitated very rapidly. Rapid precipitation encourages the formation of very fine particles and there were indications that these gold particles could be absorbed if they came into contact with the cupel surface before they were alloyed with lead. The more complete recovery of the smaller amounts of gold supports this suggestion. Further evidence was obtained by cupelling artificial buttons prepared from a constant amount of gold solution and varying amounts of lead. The losses were larger with decreasing proportions of lead.

To verify that the loss of gold was into the cupel, a fire assay of the used cupels was made, using flux E. The gold recovered was 90% of that lost during cupellation.

In an attempt to avoid the losses experienced when using gold solutions, the gold was precipitated before its addition to the lead boat. Lead powder and sulphur dioxide did not give improved results but silver powder gave quite an accurate and consistent gold recovery. Varying amounts of silver gave equal accuracy and 50 mg were sufficient for complete recovery of 20 mg of gold. The gold chloride solution was placed in a small beaker and silver powder was added. After 2 hr of heating on a steam-bath, the contents of the beaker were transferred to a lead boat, with careful washing. The solution was evaporated and the boat was folded and cupelled as before.

These cupellation and parting experiments showed that there was complete recovery of gold by the procedures described but the loss of gold to the cupel when using artificial buttons prepared with gold solutions is quite significant, because standards for spectrographic and other procedures are often prepared in this manner. Though the losses are negligible for a few micrograms, they can be considerable for larger amounts and unless some corrective measure such as prior precipitation is taken, the buttons used for standards are best prepared by adding gold metal to lead foil or by doing the complete fire assay.

Sampling

The precision and accuracy of any method depends on the effectiveness of the sampling procedure. The ore sample received in the laboratory usually weighed less than 100 lb and was crushed and ground to 100–200 mesh. The ore was split by hand riffling and two of the portions accepted if their weights differed by less than 1%; otherwise the portions were recombined and the process repeated.

When the sample weight had been reduced to a convenient amount, the ore was placed on a large cellophane sheet and rolled thoroughly by lifting alternate corners of the sheet, taking care to avoid losses because of too vigorous rolling. The ore was spread evenly on the cellophane and the surface marked into 1 in. squares. The sample required for an assay was obtained by taking a small segment from each square, making sure that each segment extended down to the surface of the cellophane.

It is apparent that true homogeneity is impossible unless the gold is a dissolved constituent in the

TABLE II.—THE DETERMINATION OF GOLD IN GOLD ORES BY FIRE ASSAY

Ore designation	#288	#293	#294	#295	#305	#7	#4
Mine	Kirkland Lake	Minto	Buffalo Ankerlite	Ashley		Ore concentrate	Patricia ore concentrate
Gold concentration*, *oz/ton*	3·56	0·762	0·460	0·604	0·328	54·54	22·96
	3·00	0·766	0·440	0·662	0·262	54·40	23·08
	3·22	0·648	0·452	0·696	0·260	55·02	23·14
	3·08	0·890	0·432	0·638	0·282		23·16
	2·96	0·782	0·440	0·880	0·322		23·00
	3·20	0·550	0·418		0·284		22·52
							22·96
Average concentration	3·17	0·733	0·440	0·696	0·290	54·65	22·96
							22·96
Average deviation	0·16	0·089	0·009	0·074	0·024	0·24	23·06
							23·14
Gold concentration, *oz/ton*	2·80	0·454	0·452	0·568	0·260		22·78
	2·88	0·760	0·446	0·738	0·276		22·30
	2·80	0·900	0·482	0·850	0·260		22·38
	3·02	0·712	0·438	0·526	0·294		
	3·16	0·762	0·500	0·660	0·224		
	3·02	0·444	0·498	0·488	0·238		
Average concentration	2·95	0·672	0·469	0·638	0·259		22·89
Average deviation	0·12	0·149	0·024	0·111	0·018		0·22

* Gold concentration was determined by the bromoaurate method.

entire ore body. Since gold commonly occurs as the native metal or as a constituent of a particular mineral, real homogeneity is not obtainable by any physical procedure. The apparent homogeneity depends on the physical nature of the noble metal, the size of the ore particles and the size of sample taken for analysis. The use of the assay ton (approximately 29 g) for the fire assay, taken from a well-mixed sample, often provides apparent homogeneity.

The determination of gold in ores by fire assay

Several gold ores were obtained from the Mining Department (University of Toronto) and those were crushed, ground and sampled as described. Two gold ore concentrates were similarly treated. Each sample was designated by a number and the originating mine was known in most cases. In addition a nickel ore, flotation concentrate and matte were also treated as described. The gold ores and concentrates were composed mainly of silicates and the nickel samples mainly of sulphides. For all samples the whole of the crushed ore passed through a 100-mesh screen and 90–100% passed through a 200-mesh screen.

The gold concentrates and ores were assayed, using flux A, by the methods previously discussed. Blanks were made by substituting an appropriate amount of silica for the ore, but these contributed only a minor amount to the gold value. The gold concentrations were determined by direct weighing of the gold residue or by dissolution and the use of either the hydroquinone precipitation or the bromoaurate colorimetric procedure. The values obtained for these ores are recorded in Table II.

The nickel matte and concentrate required nitre assays and flux B was used for the matte and fluxes B, C and D were used for the concentrate. The assay was conducted as described for the standard gold samples. Blanks were provided by an appropriate amount of the following mixture: silica 12 g, iron sulphide 12 g, copper and nickel sulphides 3 g of each. Gold was determined by the bromoaurate colorimetric procedure.

Preliminary assays of the nickel concentrate gave unexpectedly high spectrophotometric values. An examination of the ultraviolet and visible spectra showed two distinct peaks in the 0·8*M* hydrobromic acid solutions, at 295 mμ and 370 mμ. These peaks corresponded to those for lead and bismuth respectively, and the bismuth peak effectively masked the bromoaurate peak at 380 mμ. The presence of microgram amounts of lead and bismuth was confirmed by several spot tests.

TABLE III.—THE DETERMINATION OF GOLD IN NICKEL ORES BY NITRE ASSAY

Sample	Gold concentration, *oz/ton*		
	Flux B	Flux C	Flux D
Flotation Concentrate	0·0130	0·0125	0·0128
	0·0123	0·0092	0·0118
	0·0115	0·0139	0·0090
	0·0164	0·0087	0·0097
	0·0087	0·0067	0·0122
	0·0121	0·0095	0·0151
	0·0160	0·0112	0·0107
	0·0117		0·0131
	0·0146		0·0093
	0·0067		0·0137
			0·0101
Average	0·0123	0·0102	0·0116
Mean deviation	0·0020	0·0020	0·0017
Copper–nickel	0·0629		
Matte	0·0660		
	0·0666		
	0·0606		
Average	0·0640		
Mean deviation	0·0023		

The presence of a small amount of lead in the silver bead is not unexpected, but normally this is removed as the nitrate during the parting procedure. Trace amounts of bismuth in the litharge are probably collected in the lead button during the nitre assay, although this was not observed for the normal assay. The supposition that the bismuth originated in the litharge is supported by the observation that interference from bismuth was observed with blanks prepared as described and even with blanks consisting only of flour and flux.

The separation of gold from bismuth and lead was easily achieved by extraction of the bromoaurate from 0·8*M* hydrobromic acid by ethyl acetate.[3] The gold was completely recovered and could be determined as the bromoaurate after evaporation of the ethyl acetate, destruction of any organic residue, and dissolution of the gold.

The values obtained for the determination of gold in the nickel matte and concentrates are recorded in Table III. The values for the gold concentrates and the nickel samples show the homogeneity achievable by the sampling method described. The results for the gold ores sampled in the same way, show that the homogeneity of these samples is quite varied, the results for some showing similar precision to those for the gold concentrates, while others show considerably larger variations.

The variations in precision emphasize that any assay of an ore is very dependent on the degree of homogeneity within the sample. It is apparent that no assay result should be accepted without some knowledge of the methods used to obtain homogeneity and that no range of acceptability may be proposed without a series of values being obtained for the particular ore.

WET EXTRACTION

Wet extraction is a term used to describe any method in which the desired constituent is concentrated into a liquid medium. This process has the advantage that the chemistry of the resulting solution can be predicted with reasonable certainty. On the other hand, the fire assay, which concentrates the gold into a solid medium, presents difficulty because of a lack of knowledge of the components of the ore and of the products occurring during the assay process.

The most common methods of commercial wet extraction of gold from ores are amalgamation and cyanidation. The recovery of gold by these methods varies with the character of the ore and the physical conditions of the extraction. For the analysis of gold in ores, a more complete extraction is required and usually involves some acid treatment. *Aqua regia* is commonly favoured as an extractant and the gold is then isolated by solvent extraction or by precipitation.

Most methods for the wet extraction of gold and its determination are designed to be field tests and thus give semi-quantitative values at best. No research report has verified the completeness of the extraction process or the efficiency of the other processes used for the purification or the gold prior to its determination. For this reason, several extraction methods were investigated for both milligram and microgram amounts of gold, and the values obtained for several gold ores by these methods were compared with values obtained by its fire assay.

EXPERIMENTAL

The wet extraction of gold

Several techniques were used to extract gold from an ore. The completeness of the extraction was evaluated by fire assaying the ore residue. The residue was mixed with an appropriate amount of flux A and with enough silica to compensate for the portion of the ore which was dissolved. The fire assay was carried out as described previously and the gold content of the residue determined by the bromoaurate method.

Extraction methods for gold

Several 15-g ore concentrate samples were treated in plastic beakers with 25 ml of hydrofluoric acid. The solution was evaporated by heating on a steam-bath and the process was repeated. The residue was dissolved in hydrochloric acid and the solution was evaporated to dryness several times to ensure removal of hydrofluoric acid. The residue was dissolved in 25 ml of *aqua regia* and the solution was diluted with 25 ml of water and filtered through Whatman No. 42 filter paper, the beaker and paper being carefully washed. The filter paper and the small amount of residue in it were fire assayed, with proper adjustment of the flour content of the flux to allow for the reducing effect of the filter paper. By comparison with the fire assay values, the extraction of gold was 99·7–99·9% complete.

A few samples of 7·5 g and 3·75 g of ore concentrate were hydrogenated in porcelain boats for 4 hr at 650° in a Vycor tube and then chlorinated for 4 hr at 700° with a slow stream of chlorine. Other samples were treated by chlorination only. Each of the samples was treated individually and after cooling, was transferred to a beaker. The inside of the Vycor tube was washed with hydrochloric acid and the washings added to the same beaker. The porcelain boat was washed free of any residue and removed from the beaker. The contents of the beaker were evaporated and then treated with 25 ml of *aqua regia*. After dilution with 25 ml of water, the contents of the beaker were filtered through Whatman No. 42 or No. 541 filter paper, and the residue was thoroughly washed. The paper and the residue were dried and then fire assayed. The extraction by hydrogenation and chlorination or by chlorination alone was calculated to be 99% complete.

Several 15-g gold ore concentrate samples were treated with 30 ml of *aqua regia* for 24 hr on a steam-bath with occasional stirring. After dilution with water, the samples were filtered through Whatman No. 42 or No. 541 filter paper, and the residual gold determined by fire assay. This extraction of gold was 99·5% complete.

The *aqua regia* extraction was repeated with the available gold ores and in this case the residue was dried in the original beaker and then treated again with *aqua regia*. The gold remaining in the residue and the gold found in the evaporated second extract were determined by fire assay. For the

gold ores which contained 100–600 μg of gold per sample, the first extraction was 98·0–99·5% complete and the final undissolved residue contained a maximum of 0·5% of the original gold.

Although the chlorination procedure gave acceptable results, it was more time-consuming than the methods involving *aqua regia* and hydrofluoric acid, and also required more extensive equipment, especially if a large number of samples were to be handled. The *aqua regia* extraction could be done with a minimum of equipment and supervision and was generally 99% efficient in a single treatment. Treatment of the ore with hydrofluoric acid removed silica and permitted a more efficient dissolution of gold. Since only negligible amounts of residue remained after the hydrofluoric acid and *aqua regia* treatments, the extraction of gold was quite complete.

The procedures described above were evaluated only for the completeness of the removal of gold from ores and not for the total recovery of the precious metal.

The separation of gold from base metals

The extraction of gold from an ore by the methods described is accompanied by simultaneous extraction of base metals. The isolation of gold by precipitation and by most solvent extraction methods is subject to interference from these base metals.

For the recovery of small amounts of gold from solutions, and for the separation of gold from most of the other elements, the co-precipitation of gold with tellurium has frequently been used.[3–6]

Nitrous oxides were removed from the *aqua regia* extract of a gold ore concentrate by evaporating it nearly to dryness several times after addition of a few ml of hydrochloric acid. The solution was diluted to 50 ml and adjusted to be 2·4–3·6*M* in hydrochloric acid; then 1–2 ml of 2% tellurous acid solution were added. The solution was heated to boiling, and 10 ml of 15% hydrazine hydrochloride solution and 40 ml of a saturated solution of sulphur dioxide were added, which caused the formation of a dark precipitate. The precipitate was also formed by bubbling sulphur dioxide through a sample solution heated on a steam-bath. The sample was digested by continued heating. The coagulated precipitate was quite coarse and easily filtered off on medium porosity sintered glass crucibles or Whatman No. 42 filter paper.

The filtrates from several ore samples treated in this way were fire assayed and indicated that the loss of gold to the filtrate was 0·1–0·3%.

Separation of gold from tellurium

The tellurium co-precipitation of gold provides a fast and efficient method for separating gold from the base metals. Unfortunately, it is difficult to determine gold in the presence of tellurium and a complete separation is often required.

The most common method of removing tellurium is to volatilize it by heating the precipitate at 600–700° in air, but it was found that an interfering residue was left which could not be removed even by prolonged heating. Since small amounts of tellurium interfere with the bromoaurate method, a more complete separation was required.

Tellurium forms a volatile hydride and it was found that hydrogenation of the precipitate for 12 hr at 650–750° successfully removed the tellurium. A shorter hydrogenation (2–3 hr) was sufficient if the bulk of the tellurium was volatilized by an initial 5-hr heating in air. Gold does not form a volatile hydride under these conditions.

The hydroquinone precipitation of gold in the presence of tellurium was developed by Seath and Beamish[6] for milligram amounts of gold. No previous report deals with the separation of microgram amounts of gold with this procedure.

The tellurium-gold precipitate was collected in a sintered glass crucible, washed thoroughly with hot water, and dissolved in *aqua regia*. The solution and washings were transferred to a beaker and evaporated to dryness after the addition of 2 ml of 2% sodium chloride solution. Any nitrous oxides were removed by alternate evaporation and addition of a few drops of hydrochloric acid. The residue was dissolved in 40 ml of 1·2*M* hydrochloric acid the and solution was heated to a gentle boil, a small piece of filter paper being used to prevent "bumping". From a small dropping tube, 1 ml of 5% hydroquinone solution was added slowly to the solution to initiate the reduction, and then 5 ml of the hydroquinone solution were added by a Mohr pipette to complete the precipitation. The solution was boiled for 30 min to coagulate the precipitate, cooled and filtered through a 7-cm Whatman No. 42 filter paper. The beaker was carefully cleaned with small pieces of filter paper as "policeman." The filter and extra paper was folded and ignited in a porcelain crucible.

The collection and separation of gold

The collection of gold by co-precipitation with tellurium and the separation of gold from tellurium by either the hydrogenation or hydroquinone methods was evaluated by the use of standard gold solutions. Standard samples containing 10 μg–1 mg of gold were treated as described after addition of 30 mg of tellurium. The combined procedures gave a recovery of about 94% for microgram amounts of gold and 98% for milligram amounts.

The wet determination of gold was evaluated by using various amounts of a gold ore concentrate

already analysed by fire assay. The results show a recovery of 80% or more for 10 μg and 95–98% for larger amounts of gold.

The wet determination of gold ores

The gold content of the five gold ores and one gold ore concentrate was determined by the wet procedure outlined. The values obtained are reported in Table IV. They are quite similar to those obtained by the fire assay, and so is the precision. Only by chance was homogeneity obtained and the degree to which it occurs may be measured by the precision of the values obtained by either the fire assay or the wet method.

TABLE IV.—THE DETERMINATION OF GOLD IN ORES BY WET EXTRACTION

Ore designation Mine name	#288 Kirkland Lake	#293 Minto	#294 Buffalo Ankerite	#295 Ashley	#305 —	#4 Patricia Concentrate
Gold concentration*, *oz/ton*	3·01	0·686	0·388	0·668	0·240	22·0
	2·85	0·976	0·424	0·728	0·296	22·0
	3·04	0·910	0·356	0·722	0·184	22·2
	3·08	0·956	0·396	0·548	0·254	22·2
	3·30	0·530	0·366	0·992		22·8
		0·568	0·366			22·4
Average concentration	3·05	0·771	0·382	0·731	0·243	22·3
Average deviation	0·09	0·176	0·020	0·101	0·031	0·2
Gold concentration*, *oz/ton*		0·932	0·404	0·894	0·248	22·0
		0·866	0·406	0·928	0·292	21·8
		0·750	0·430			21·4
Average concentration		0·849	0·413	0·911	0·270	21·7
Average deviation		0·066	0·011	0·017	0·022	0·2

* Determined colorimetrically by the bromoaurate procedure.

DISCUSSION

The wet extraction method provides an alternative to the fire assay which is especially useful in those cases when the fire assay values are in doubt. While the fire assay requires the use of a special assay furnace and associated equipment, the wet method may be carried out with normal laboratory equipment. The fire assay procedures may be carried out rapidly and with little attention but the wet method does not have these advantages. The wet extraction, however, requires less knowledge of the ore composition, whereas the influence of the nature of the noble metal minerals is one of the questionable aspects of the fire assay. Because the mechanically mixed components are not known with any certainty, the claim has occasionally been made that the fire assay is ineffective for particular ores. Wet extraction is always effective.

NEUTRON ACTIVATION ANALYSIS

Neutron activation analysis techniques are most frequently applied for submicrogram amounts of constituents, and in this range, no tool of comparable value exists. While this high sensitivity is an outstanding advantage, it is also important that errors arising from contamination during processing should be eliminated. After irradiation,

only the radioactive constituent is determined and thus milligram amounts of inactive constituent may be added to serve as a carrier for the trace amount of radioactive material. The carrier permits the use of conventional techniques, and if complete isotopic exchange can be assumed, the chemical yield can be used to correct for any losses of active constituent during the procedure. The nuclear properties of a radioactive isotope such as half-life, beta energy and gamma energy provide for its unequivocal identification.

The major disadvantages of activation analysis are the need for irradiation facilities and the fact that the method makes no distinction between different oxidation states.

Many of the problems arising in activation analysis are the result of an uncritical acceptance of the chemical yield as an alternative to acceptable chemical methods. In addition, the problem of securing a representative sample of the size required for activation analysis increases the difficulty of obtaining results comparable to those of ordinary chemical methods in concentration ranges where both may be applied. This is a particularly important factor in the determination of gold and other noble metals in ores, particularly when, as usual, the homogeneity of the sample is in doubt.

Various explanations have been offered for the lack of precision of some activation methods and for the discrepancies between the values obtained by some activation procedures and by other medthods for the determination of gold in ores, but no acceptable evaluation of the neutron activation method for gold ores has been recorded.

EXPERIMENTAL

Activation of gold standards

The precision of the activation analysis technique developed was evaluated by the use of gold standards. These samples, containing 0·05–5 μg of gold were prepared by evaporating weighed amounts of standard gold solution in 3–5 mm quartz tubes. The tubes were sealed by fusing with an oxygen torch, and were wrapped in aluminium foil and placed in an aluminium irradiation capsule. The samples were irradiated in the McMaster Reactor (Hamilton, Ontario, Canada) at a flux of approximately 5×10^{12} n/cm^2/sec for 3–12 hr.

The irradiated samples were transferred from the capsule to individual plastic beakers and treated by the procedure described below for ore samples. The results showed that an average deviation of 2–8% may be expected.

The similarity of the specific activity for varying amounts of gold indicates that there is no self-shielding problem with microgram amounts of gold.

Activation analysis of gold in ores

The activation analysis technique only permits the use of a small sample, usually less than 0·5 g, so the preparation and sampling of an ore is very important. The degree of homogeneity is likely to be much larger with small samples than with 30-g samples.

To provide as much uniformity as possible, the sample for analysis was removed from 30 g of the ore, treated as described for the fire assay but marked into $\frac{1}{2}$ in. squares on the cellophane. The samples were added to tared quartz vials which were centrifuged to pack most of the ore in the bottom. Any residual powder in the upper portion of the vial, which might be lost on sealing, was removed with a small piece of filter paper. The vial was re-weighed and then sealed. Each set of ore samples together with at least one standard was placed in an aluminium capsule and irradiated for 3–12 hr.

The nickel ores as well as the gold ores could be completely dissolved in a mixture of nitric and hydrofluoric acids (1 + 3). These dissolved irradiated samples were filtered and the filter was washed thoroughly. Examination of the paper with a multi-channel gamma spectrometer showed only minor amounts of activity of various energies similar to those of the sample solution, which suggests that some solution was retained on the paper.

The sample vials were opened in a glove-box after irradiation, and most of the material removed by gentle tapping. Attempts were made to ensure complete removal of sample by washing the vial with several portions of acid. Although this technique has been generally used, it seemed to be subject to error. To eliminate the possibility of loss during opening and discarding the vials, they were

placed in 50-ml polypropylene beakers and dissolved in hydrofluoric acid. After the removal of the silica, an aliquot of a standard gold solution was added to each sample and the solution was evaporated to dryness. The residue was treated twice with 10 ml of nitric and hydrofluoric acids (1 + 3) and thrice with 10 ml of *aqua regia*, with evaporation to dryness after each addition. The residue was dissolved in 5 ml of *aqua regia* and 1 ml of 5% sodium chloride solution was added. Nitrous oxides were removed by evaporating the solution to a small volume several times after the addition of a few drops of hydrochloric acid. This sample solution was diluted to 25 ml with 3*M* hydrochloric acid. Then 50 mg of tellurium (as tellurous acid solution) were added and sulphur dioxide was bubbled through the solution until the tellurium was precipitated and coagulated. The presence of nitrous oxides interfered with and delayed the precipitation, but prolonged treatment with sulphur dioxide eventually produced elemental tellurium. The solution was filtered through a sintered glass crucible and the beaker and crucible were washed thoroughly. The filtration was done in a fume hood or with the operator wearing a proper gas-mask, because of the risk from prolonged exposure to the sulphur dioxide fumes. The gas could have been boiled out, but the plastic beakers did not permit boiling, and the delay might have led to considerable decay of the radioactivity. Fire assay showed the filtrates to contain less than 1% of the total gold activity.

The tellurium precipitates from several nickel concentrate samples were examined with a gamma scintillation multi-channel analyser and were found to contain radioactive isotopes of gold, antimony and selenium. The samples required separation because the activity of selenium interfered with that of gold and because the inactive tellurium prevented the determination of chemical yield.

Although preliminary trials showed that gold could be separated radiochemically pure from antimony and selenium by ethyl acetate extraction of the bromoaurate, the partial extraction of tellurium prevented a yield determination. The hydroquinone precipitation provided a separation of gold from selenium, tellurium and antimony. The tellurium precipitate was dissolved in *aqua regia* and the crucible washed clean. The sample and washings were treated as described earlier for the separation of gold from tellurium (p. 7). The filtrates from this separation were examined and showed that varying amounts of gold were lost because of incomplete precipitation. A longer digestion period of 1 hour or more gave more consistent and complete separation. The filtrates from nickel concentrate samples contained radioactive selenium and antimony but those from gold ores showed only negligible amounts of activity.

The gold residue was dissolved in a few drops of *aqua regia*, sodium chloride was added and nitrous oxides were removed by evaporations. The final solution in a few drops of hydrochloric acid was diluted to 25 ml with 0·8*M* hydrobromic acid. One aliquot of this solution was used to determine the bromoaurate concentration spectrophotometrically at 380 mμ, and another to determine the activity of the gold-198 with a well-type, single channel, gamma scintillation counter. The range of energies counted was 0·39–0·43 MeV with the peak for gold occurring at 0·41 MeV. The gamma spectrum and a half-life measurement both showed that the gold was radiochemically pure.

The chemical yield was calculated for each sample and used to correct for losses during the procedure. The recovery of gold was 90–100% for those samples given a longer digestion period to precipitate gold, but varied more widely for the others. The losses of gold may be the result of the remote handling procedures required for radioactive materials; the use of tongs, rubber gloves, *etc.*, does not promote accurate manipulation. The plastic beakers used for the ore dissolution show a tendency to retain some activity although they have no observable preference for gold. The losses to the beaker are dependent on the condition of the inner surfaces and probably beakers should be discarded after use to avoid any carry-over of active materials and to provide more uniform conditions.

The amount of gold was calculated by comparison of the activity of samples and standards, corrected for the chemical yield. The values obtained for several gold ores and nickel ores are recorded in Table V.

The results for gold ore No. 294 show reasonable consistency and quite good agreement with values obtained by other methods. However, the precision given by the activation analysis techniques for other gold ores is very poor. Values of 0·2–1·3 oz/ton for the same ore indicate the magnitude of the problem of sample homogeneity in the determination of gold. The values obtained for gold in the nickel matte, concentrate and ore indicate that the gold is considerably more homogeneously distributed in these samples.

The neutron activation analysis technique which was developed avoided losses due to incomplete removal of sample from the irradiation vial or to incomplete dissolution of the sample. Only small amounts of gold were lost because of incomplete co-precipitation with tellurium or by hydroquinone and these losses could be corrected for on the basis of the chemical yield. Isotopic homogeneity was encouraged by the similar treatment given the carrier and the active gold. No appreciable losses of radioactive gold were observed and the chemical yield indicates only small losses of the carrier gold. The similarity of the specific activity for different amounts of irradiated gold sample indicated that there was no self-shielding effect for the amounts of gold used and that quite probably isotopic homogeneity had been obtained. The effect of the matrix could not be properly evaluated because

TABLE V.—THE DETERMINATION OF GOLD BY NEUTRON ACTIVATION

Ore designation	Mine	Weight of sample taken, *mg*	Yield, %	Specific* activity, *cps/g*		Gold content, *oz/ton*	Average† gold *oz/ton*
#294	Buffalo Ankerite	61·5	93	1·18	× 10^4	0·495	
		56·1	91	0·822		0·345	
		82·6	95	1·34		0·558	
		55·1	92	0·935		0·393	
		49·1	94	1·02		0·426	0·422 ±
		62·2	93	0·746		0·313	0·071
#295	Ashley	66·2	96	1·14	× 10^4	0·190	
		68·9	97	3·76		0·629	
		67·7	96	5·56		0·927	
		56·2	90	3·28		0·546	0·663 ±
		84·4	93	1·99		0·372	0·306
		58·4	92	7·88		1·317	
		14·7	75	1·45	× 10^3	0·115	
		12·1	61	0·96		0·076	0·242 ±
		11·7	61	6·58		0·534	0·195
		52·2	80	2·40	× 10^3	0·088	
		72·5	52	1·48		0·054	
		55·9	24	0·82		0·030	0·079 ±
		47·3	87	2·10		0·077	0·031
		40·2	55	4·03		0·147	
#305	—	47·9	92	7·68	× 10^4	1·278	
		42·9	90	1·30		0·216	
		41·6	58	2·00		0·334	
		36·2	91	1·70		0·284	
		45·6	85	8·76		1·461	0·630 ±
		49·6	90	1·26		0·210	0·493
		41·6	75	3·63	× 10^3	0·298	
		13·6	49	23·8		1·956	0·821 ±
		33·6	58	2·54		0·210	0·756
		76·6	89	4·03	× 10^3	0·148	
		83·9	91	13·3		0·486	0·233 ±
		66·6	23	1·84		0·067	0·168
Copper–Nickel Matte		188·2	57	3·48	× 10^3	0·0579	
		179·4	92	3·50		0·0582	
		161·7	89	3·96		0·0660	
		177·1	91	3·88		0·0648	
		136·2	83	3·92		0·0654	0·0634 ±
		177·3	35	4·06		0·0678	0·0035
		253·9	90	1·55	× 10^3	0·0651	
		336·4	97	1·51		0·0630	
		196·5	83	1·53		0·0639	
		151·0	77	1·48		0·0618	
		169·1	86	1·44		0·0603	0·0632 ±
		171·7	94	1·55		0·0648	0·0015
Flotation concentrate		138·4	98	56·0		0·0135	
		129·7	100	57·5		0·0138	
		127·5	99	55·2		0·0133	0·0120 ±
		135·3	95	29·5		0·0072	0·0023

TABLE V.—(*cont'd*)

Ore designation	Mine	Weight of sample taken, *mg*	Yield, %	Specific* activity *cps/g*	Gold content, *oz/ton*	Average† gold *oz/ton*
		137·4	57	55	0·0056	
		120·8	83	89	0·0091	
		109·8	77	80	0·0082	
		141·1	88	193	0·0197	0·0103 ±
		58·1	63	89	0·0091	0·0037
		156·2	48	90	0·0062	0·0124 ±
		132·8	67	272	0·0185	0·0062
Copper–Nickel ore		196·3	89	52·4	0·00087	
		140·4	60	65·4	0·00109	
		137·6	90	39·4	0·00066	
		211·4	91	38·6	0·00064	
		172·0	65	58·6	0·00098	0·00103 ±
		204·6	93	116·6	0·00194	0·00032

* Average gold content ± the average deviation.

of the variations occurring with the ore samples, but irradiation of ore samples salted with a gold standard indicated no major variations.

The activation procedure described required approximately three days for completion although as many as 30 samples were done at one time. The procedure could be shortened if a better method of separating gold and tellurium could be devised. The separation would be unnecessary if there was no selenium in the sample and if the chemical yield was 100%. The technique could also be made more rapid by eliminating the dissolution of the quartz vial although this might be a source of error. The replacement of filtration by the use of the centrifuge would reduce the time required for filtration and for the subsequent treatment. While each change in technique would decrease the time required for a determination, most of those suggested would also increase the losses of gold, but if the chemical yield could correct for these losses, the revised procedure could be used. Without a careful examination no variation can be unconditionally recommended.

The activation analysis procedure as outlined gives a radiochemically pure sample with a high yield and provides accurate and precise values for materials for which representative irradiation samples can be taken.

CONCLUSIONS

The amount of gold in ores may be estimated by fire assay, wet extraction or neutron activation by the procedures described.

The fire assay is the fastest and most efficient method for multiple and routine analysis of ores, but requires considerable equipment and a flux suitable for the individual ore. This technique may be used with large amounts of ore and thus is relatively insensitive to the homogeneity of the gold distribution in the ore. For milligram and microgram amounts of gold, the losses by each of the procedures of the fire assay were found to be negligible. This method remains the least understood on a theoretical basis and considerable improvement in the existing techniques for devising a flux and for predicting losses might be expected if this knowledge was forthcoming.

The wet extraction may be used with a variety of sizes of sample and permits a laboratory, without special equipment, to determine gold in ores. Although the ores used for the evaluation of the method may have given fortuitously good results, suitable variations of the dissolution technique should provide similar results. The method which was developed could be improved by a more efficient technique of separating gold from tellurium or by methods of determination which tolerate large amounts of tellurium. Although the procedures are time-consuming, many samples

can be treated simultaneously and only negligible losses are involved for milligram and microgram amounts of gold. The wet extraction provides an alternative method for ores which present unusual collection problems for the fire assay.

The neutron activation analysis technique involved a series of treatments of the irradiated sample similar to those used in the wet extraction method. The methods were proved to be quite efficient by the use of radioactive samples. The values obtained for a variety of ores indicated the difficulty in obtaining a representative sample of the small size required. The advantage of the method was shown by the determination of less than 0·005 μg of gold. In addition, the activation technique gave accurate values for gold in a sample for which the fire assay gave erroneous results because of an interference with the colorimetric method. If the limitations imposed by inhomogeneity of the sample are taken into account, neutron activation may be used for a wide variety of gold materials,

The results of this work indicate the accuracy and precision obtainable with each procedure and emphasize the serious effect of the inhomogeneity of distribution of gold.

Zusammenfassung—Die Fehler, die bei Flammenproben-, nassen Extraktions- und Neutronenaktivierungsmethoden auftreten, werden ermittelt, die Richtigkeit und Genauigkeit dieser Methoden verglichen und eine Methode zur Bestimmung der chemischen Ausbeute bei der Aktivierungsanalyse von Gold in Erzen und Konzentraten angegeben.

Résumé—On évalue les erreurs liées aux méthodes de dosage par grillage, extraction par voie humide et activation de neutrons, compare la justesse et la précision de ces méthodes, et présente une méthode pour déterminer le rendement chimique dans le dosage par activation de l'or dans les minerais et concentrats.

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USE OF THENOYLTRIFLUOROACETONE FOR THE DETERMINATION OF MANGANESE BY ACTIVATION ANALYSIS

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Summary—A new procedure for the substoichiometric extraction of bivalent manganese by thenoyltrifluoroacetone into ethyl acetate has been developed and used in activation analysis. The value of the extraction constant has been found to be $3{\cdot}1 \times 10^{-6}$; the pH range in which the extraction can be performed is 7·8–9·2. The influence of oxalate, citrate, tartrate, fluoride and cyanide ions has been studied. A selective substoichiometric extraction of manganese in the presence of Zr, Hf, Nb, Th, Fe and Sc is possible at pH 8–8·5, tartrate and fluoride being used as masking agents. Copper and cobalt can be screened by ammonia and cyanide respectively. The method has been used for the determination of manganese in biological materials, potassium fluoride and zirconium.

ACTIVATION analysis has been widely used for the determination of manganese because the cross-section and half-life of its isotopes make the determination highly sensitive. In some simple cases the determination can be performed non-destructively. However, in most cases manganese has to be separated before the activity is counted. In general, use is made of the precipitation of manganese dioxide for the separation and isolation of manganese.[1,2,3] Extraction of tetraphenylarsonium permanganate has been used[4] for the determination of ^{56}Mn in ^{56}Cr. The substoichiometric extraction of tetraphenylarsonium (or tetraphenylphosphonium) permanganates has been suggested by Růžička and Zeman.[5] However, a preliminary extraction of manganese with sodium diethyldithiocarbamate into chloroform is recommended by these authors. A simple method for the substoichiometric extraction of manganese thenoyltrifluoroacetonate into ethyl acetate and its use in activation analysis is suggested here.

EXPERIMENTAL

Apparatus

Gamma-spectrometer, 200-channel, Intertechnique SAI 332 (Intertechnique, Versailles, France) with NaI(Tl) crystal 1 × 1·5 in.

Decadic scaler (ZVIL Plzeň, Czechoslovakia) with well-type NaI(Tl) crystal 1 × 1·5 in. Multoscop pH-meter (Labora n.p., Czechoslovakia) with a combined electrode (Metrohm, Herisau, Switzerland).

Reagents

Manganese carrier solution. An aqueous solution of manganese(II) sulphate, containing 1 mg of manganese/ml. A part of this solution was labelled with carrier-free ^{52}Mn.

Standard manganese solution. Prepared by diluting the carrier solution to give a final concentration of 0·022 μg of manganese/ml.

Buffer solution. Ammonium acetate solution, 20%—ammonia.

Masking solutions. Sodium tartrate solution, 10%. Potassium fluoride solution, 20%.

Thenoyltrifluoroacetone (TTA). Ethanolic solution of TTA, 0·11*M*. Ethyl acetate solution of TTA, 0·2*M*. Ethyl acetate was purified according to the method described in the literature.[6] All reagents used were *pro analysi* or pure reagent grade.

Irradiation

All irradiations were carried out at a neutron flux of about $7{\cdot}5 \times 10^{12}$ neutrons.cm^{-2}.sec^{-1} for 2 hr. Polythene capsules containing samples and sealed capsules holding 4 ml of standard solution were irradiated in the same irradiation can.

Determination of the extraction constant

Five ml of aqueous carrier-free solution of ^{52}Mn were adjusted to the required pH with hydrochloric acid or potassium hydroxide. The ionic strength was adjusted to 1 by addition of potassium chloride. The solution was extracted with 5 ml of 0·2*M* TTA in ethyl acetate. After the extraction the pH was measured again and aliquots of the aqueous and organic phases were taken for activity counting. The extraction curve is shown in Fig. 1. The extraction constant was calculated from the

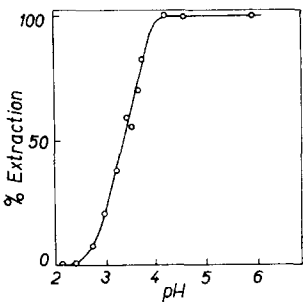

FIG. 1.—Extraction of carrier-free ^{52}Mn by 0·2*M* TTA in ethyl acetate, as a function of pH.

values of the distribution ratio ranging from 0·1 to 10 according to the relationship

$$K = q\frac{[H^+]^2}{[HTTA]^2}$$

where q is the distribution ratio.

Development of procedure

The pH region in which optimum substoichiometric extraction can be performed was estimated first. Two ml of the carrier solution (labelled with ^{52}Mn) were diluted to 30 ml, the pH was adjusted with acetic acid or ammonia and 0·5 ml of ethanolic TTA solution was added. At higher pH values, about 10 mg of hydroxylamine hydrochloride were added to prevent oxidation of manganese(II). The solution was extracted with 10 ml of ethyl acetate for 2–3 min. The time required to complete the extraction was found experimentally. The activity of the aqueous phase was determined by means of a well-type scintillation crystal. The pH region (7·8–9·2) over which the extraction is complete is illustrated in Fig. 2.

The reproducibility of the substoichiometric extraction was verified both by extractive radiometric titration of a carrier solution (labelled with ^{52}Mn) with TTA and by titration of TTA with the labelled carrier solution. The titration procedure was the same as that described earlier.[7] An example of the latter titration at pH 8·5 is shown in Fig. 3.

Influence of masking reagents

Extractive radiometric titrations were used for the study of the influence of masking agents such as tartaric acid, oxalic acid, citric acid, fluoride and cyanide on the substoichiometric extraction of manganese with TTA. The results are presented in Table I. The influence of zirconium, hafnium, thorium, iron, scandium, antimony, copper and cobalt in the presence of the masking agents was studied in the same way.

Procedure

Irradiated material was dissolved as follows: potassium fluoride in water, ash from biological samples in hydrochloric acid, zirconium and aluminium in a mixture of hydrofluoric and nitric acids. Two ml of carrier solution, 3 ml of 10% tartaric acid solution, 3 ml of 20% potassium fluoride

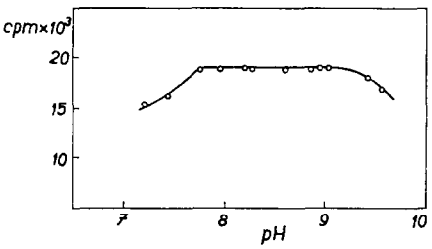

FIG. 2.—The substoichiometric extraction of manganese(II)-thenoyltrifluoroacetate, as a function of pH.

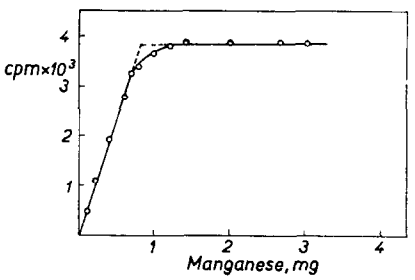

FIG. 3.—Radiometric titration of TTA with manganese(II) at pH *ca.* 8·5.

TABLE I.—THE INFLUENCE OF MASKING REAGENTS ON THE SUBSTOICHIOMETRIC EXTRACTION OF MANGANESE

Masking reagent	Amount of reagent (*mg*) required to decrease the extent of extraction by	
	1%	5%
Citric acid	75	100
Tartaric acid	650	800
Oxalic acid	200	250
Potassium cyanide	160	190
Potassium fluoride	>5000	

solution and 10 mg of hydroxylamine hydrochloride were added successively and the pH was adjusted to 8–8·5; 0·5 ml of ethanolic solution of TTA was added (corresponding to about 70% of the manganese content) and the solution was extracted for 2–3 min with 10 ml of ethyl acetate. After separation of the phases, the γ-spectrum of the organic phase was measured with a 200-channel analyser. The same procedure was performed with the standard sample. By comparison of the areas under the 0·84 MeV photopeak of the sample and the standard, the manganese content was determined.[8]

RESULTS AND DISCUSSION

TTA has been successfully used for the colorimetric[9] and flame photometric[10] determination of manganese. According to De and Rahaman[9] the region of complete extraction of manganese thenoyltrifluoroacetonate with a mixture of benzene and acetone begins at pH 6·7. Cobalt(II) and EDTA interfere with the colorimetric determination. Iron, zirconium and thorium are first extracted from a citrate medium. The

majority of metallic ions can be masked by a mixture of tartaric and hydrofluoric acids according to Johnson and Lott,[10] but cyanides show a slight interference.

The region of complete extraction has been found to be within the pH range 7·8–9·2. In the presence of ammonium acetate no manganese(II) hydroxide is precipitated at pH 9·5 even after 5 hr. However, a reducing reagent, such as hydroxylamine hydrochloride must be added to prevent the oxidation of manganese(II) to manganese(III). The extraction equilibrium is attained within 2–3 min. The influence of oxalic, tartaric and citric acids, fluoride and cyanide on the substoichiometric extraction is summarized in Table I. The error exceeds 5% only if the concentration

TABLE II.—THE DETERMINATION OF MANGANESE (MEAN VALUES FROM THREE DETERMINATIONS)

Sample	Manganese found (mean of 3 determinations)	
	μg	ppm
Zirconium (pure)	$5·9 \times 10^{-3}$	$5·8 \times 10^{-3}$
Aluminium (zone-refined)	$6·0 \times 10^{-4}$	$1·05 \times 10^{-2}$
Biological material (fish)	2·24	40·0*
Potassium fluoride	$2·7 \times 10^{-3}$	0·1

* Relative to ash content.

of cyanide is greater than 5·5 mg/ml. On the other hand, manganese thenoyltrifluoroacetonate is not back-extracted by cyanide. Use was made of these results for the selective determination of manganese in the presence of elements with higher extraction constants.[11] Manganese can be selectively extracted from a tartrate or fluoride

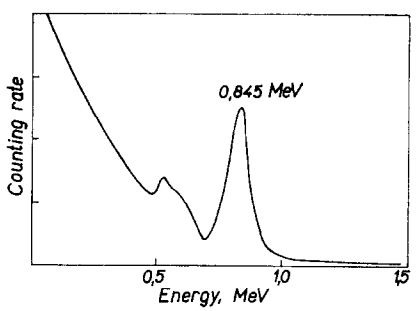

FIG. 4.—The γ-spectrum of ^{56}Mn after separation from potassium fluoride by TTA.

medium at pH 8–8·5 even in the presence of zirconium, hafnium, niobium, thorium, iron, scandium and antimony. Ammonia prevents copper and cobalt from being extracted. These ions can also readily be removed from the organic phase by a 1% cyanide solution. Carrier-free lead and thallium interfere neither with the determination of the chemical yield nor with the γ-spectrometric determination of manganese (both being pure β-emitters).

The extraction constant has been found to be $3·1 \times 10^{-6}$ (the mean value of 8 independent extractions with ethyl acetate). The recently published value[12] of the extraction constant for a mixture of benzene and acetone is 3×10^{-7}.

In Table II results are shown for analyses of potassium fluoride, zirconium and ash from fish.

The γ-spectrum of the TTA–Mn extract is shown in Fig. 4. The method described in the present communication was also used for the determination of the manganese concentration in the target, water, and reagents used in the production of ^{52}Mn by the ^{52}Cr(d, 2n)^{52}Mn nuclear reaction. These results will be published elsewhere.[13]

The method is very simple and no preliminary separations are required. The time necessary for carrying out the chemical treatment depends mainly on the time required for the dissolution. The separation itself (including the adjustment of the pH) takes less than 10 min. The maximum sensitivity attainable (5×10^{-11} g) is in agreement with other published results.[14]

Résumé—On a élaboré et utilisé dans l'analyse par activation une nouvelle méthode pour l'extraction substoechiométrique du manganèse bivalent par la thénoyltrifluoracétone en acétate d'éthyle. On a trouvé que la valeur de la constante d'extraction est de $3{,}1 \times 10^{-6}$; on peut effectuer l'extraction aux pH compris entre 7,8 et 9,2. On a étudié l'influence des ions oxalate, citrate, tartrate, fluorure et cyanure. Une extraction substoechiométrique sélective du manganèse en présence de Zr, Hf, Nb, Th, Fe et Sc est possible à pH 8–8,5, le tartrate et le fluorure étant utilisés comme agents de dissimulation. Le cuivre et le cobalt peuvent être masqués par l'ammoniaque et le cyanure respectivement. On a utilisé la méthode pour le dosage du manganèse dans les matériaux biologiques, le fluorure de potassium et le zirconium.

Zusammenfassung—Eine neue Vorschrift zur substöchiometrischen Extraktion von zweiwertigem Mangan durch Thenoyltrifluoraceton in Essigester wurde entwickelt und bei der Aktivierungsanalyse verwendet. Die Extraktionskonstante wurde zu $3{,}1 \cdot 10^{-6}$ ermittelt. Die Extraktion kann im pH-Bereich 7,8–9,2 vorgenommen werden. Der Einfluß von Oxalat, Citrat, Tartrat, Fluorid und Cyanid wurde untersucht. Mit Tartrat und Fluorid als Maskierungsmitteln läßt sich Mangan selektiv substöchiometrisch in Gegenwart von Zr, Hf, Nb, Th, Fe und Sc bei pH 8–8,5 extrahieren. Kupfer und Kobalt können durch Ammoniak bzw. Cyanid maskiert werden. Die Methode wurde zur Bestimmung von Mangan in biologischen Materialien, Kaliumfluorid und Zirkonium verwendet.

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INORGANIC POLAROGRAPHY IN ORGANIC SOLVENTS—II

POLAROGRAPHIC EXAMINATION OF THE MOLYBDENUM(V) THIOCYANATE COMPLEX IN DIETHYL ETHER

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Summary—A procedure involving the solvent extraction of molybdenum(V) thiocyanate into diethyl ether followed by a direct polarographic examination of the organic phase offers a selective method for the determination of molybdenum down to 0·5 ppm. Only molybdenum, amongst 21 elements examined, is observed to give a reduction wave under the recommended conditions. The method is evaluated with respect to various experimental factors and is applied to the determination of molybdenum in mild and alloy steels.

THE previous communication in this series[1] showed some of the advantages to be obtained by carrying out a polarographic examination of an organic phase following solvent extraction. The extraction system described below, when used in conjunction with polarography, has an enhanced selectivity. This arises because, although certain species are reduced at a dropping mercury electrode in aqueous solution, they do not necessarily give polarographic waves in an organic solvent. The direct application of polarography to the examination of a diethyl ether phase used for solvent extraction of metal-thiocyanate complexes has been found to give a selective method for the determination of molybdenum(V).

The method has been tested on a number of B.C.S. mild and alloy standard steels, and has many advantages over others previously described. For instance, the method used by Haight,[2] although sensitive, depends on the use of a catalytic wave and measurements are made from a non-linear calibration curve. In addition, the careful control of experimental conditions and the absence of certain anions is essential. A method devised by Wolfson[3] for molybdenum in nickel alloys used a citric acid–sulphuric acid supporting electrolyte, but is interfered with by large amounts of iron and copper. Parry and Yakubic[4] described a method suitable for steels, using a tartrate supporting electrolyte. However, only synthetic mixtures were examined and even then only after removal of iron and chromium. The method evolved by Stackelberg *et al.*[5] can only be used after the chemical separation of molybdenum from all the other alloying elements.

Other potentially useful polarographic reduction waves for molybdenum involve the use of either a non-linear calibration curve,[6] a catalytic wave[7] or the extensive removal of other elements.[8,9]

The most widely used method for determining molybdenum is a spectrophotometric one,[10] by means of the red colour produced with thiocyanate. However, we have found that interference is given in certain instances; for example the high chromium

content (5·03%) of the alloy steel B.S.C. No. 241/1 produces an intense green colour under the recommended conditions and interferes in the spectrophotometric method.

EXPERIMENTAL

The apparatus used was an Elliot Polarograph Model 200 with a dropping mercury electrode. Unless otherwise stated the operating conditions were as follows: rate of potential increase 0·5 V/100 sec, drop time 3·4 sec, height of mercury reservoir 60 cm, mercury flow-rate 2·2636 mg/sec, temperature *ca.* 18°, no damping or counter current. An internal mercury pool anode was used and de-aeration was achieved by bubbling nitrogen through a 5-ml sample for 2 min. Provided this time is not exceeded, there is a negligible reduction in volume.

A mercury seal was used instead of the more usual water seal to prevent re-absorption of oxygen. All chemicals were analytical grade unless otherwise stated.

Preliminary polarographic investigation

The solvent extraction procedure followed was as described by Morrison and Freiser.[11] The aqueous phase (25 ml) was made 10^{-3} *M* in metal ions, *ca.* 0·5*M* in hydrochloric acid and *ca.* 2*M* in ammonium thiocyanate (by addition of 2·5 ml of a saturated aqueous solution). Extraction was carried out with 15 ml of diethyl ether (G.P.R.*) and the resulting organic phase, after the addition of 5 ml of a 0·5*M* lithium chloride (G.P.R.) solution in methanol (G.P.R.), was diluted to 25 ml with methanol. This solution was de-aerated with oxygen-free nitrogen and polarographed, the instrument sensitivity being 10 μA/full scale deflection. The efficiency of the extraction was checked by examining the aqueous phase.

Table I shows the half-wave potentials of the reduction waves in the organic phase (column 5) together with those obtained in an aqueous phase before and after complex formation (columns 2 and 3 respectively). All the metal ions known to be extracted under these conditions were examined.

Most of the metal ions examined, and their thiocyanate complexes, give polarographic waves in acidic aqueous solution. However, in the organic phase only those due to Fe(III) and Mo(V) and Mo(VI) are produced. The thiocyanate complexes of Ga, In, Sn(IV) and U(VI) are not reduced in the organic phase, although they give waves in aqueous solution and are certainly extracted to some extent (*ca.* 70%, 70%, 99% and 40% respectively).[11] Consequently, the direct application of polarography to the organic phase gives a greater degree of selectivity. It can be seen from Table I that the reduction waves for some metal-thiocyanate complexes in aqueous solution (column 3) occur at more positive potentials than those for the corresponding aquo- or chloro- complexes (column 2), *e.g.*, As(III), Bi, Ga, Mo(V), Mo(VI), Sb(III), Sn(IV), Ti(IV), U(VI) and V(V). This effect can be used to advantage with an element such as gallium which does not give a reduction wave in acidic aqueous solution. It can also be used to obtain a separation of the reduction waves for mixtures of metal ions, *e.g.*, Bi and Sb(III), As(III) and Mo(V) or Mo(VI). In addition, the three Mo(V) reduction waves in acidic aqueous solution are ill-defined and the individual wave-heights are very small. As a result, they are of no use either for theoretical or analytical purposes. However, the extracted thiocyanate complex gives a well defined wave with a diffusion current approximately equal to the sum of the three waves in aqueous solution. Without information on parameters of the Ilkovic equation for the aqueous and non-aqueous systems, it is difficult to make a sound theoretical interpretation of this phenomenon, but from the analytical point of view the summation into a single, much larger, wave is highly advantageous.

The available potential range under these conditions was 0·0–0·9 V *vs.* mercury

* General purpose reagent.

pool and was controlled by the anodic dissolution of mercury and the catalytic reduction of hydrogen. The cell resistance was approximately 500 Ω so that the iR drop was negligible in these experiments.

The addition of ascorbic acid to the aqueous phase reduces Fe(III) to Fe(II) and was found to render the combination of techniques specific for Mo(V).

The following experimental variables and their effects on the molybdenum(V) thiocyanate reduction were examined.

Organic solvents

An aqueous solution of the molybdenum(V) thiocyanate complex was equilibrated, as above, with a number of organic solvents, *viz.*, diethyl ether, isobutyl methyl ketone, amyl acetate, toluene, chloroform and carbon tetrachloride. Only the first three solvents extracted the complex and gave solutions yielding polarographic reduction waves. Isobutyl methyl ketone also extracted 65% of copper(I) and (II) which gave rise to a wave with $E_{\frac{1}{2}}$ −0·3 V *vs.* mercury pool. All efforts to prevent the extraction of copper, and its reduction, by the addition of complexing agents were unsuccessful. Amyl acetate did not extract copper, but did extract tin(II) quantitatively. In the presence of molybdenum an additional wave with $E_{\frac{1}{2}}$ −0·45 V was given and the molybdenum(V) wave had a very large maximum which could not be suppressed. As with copper, it was not possible to prevent the extraction of tin(II) whilst allowing the extraction of molybdenum(V). In the absence of molybdenum, no wave for tin(II) was observed in the organic phase, although examination of the aqueous phase showed it had been extracted quantitatively. The height of the tin(II) wave and the molybdenum maximum both increased with increasing concentrations of tin(II).

Both solvents extracted iron(III) quantitatively, but not iron(II) and thus diethyl ether was selected for further investigation because of its greater selectivity.

Hydrochloric acid concentration

The concentration was varied between 5*M* and 0·001*M* and its effect on the extraction and half-wave potential of the molybdenum(V) thiocyanate complex was evaluated. The polarographic wave moved towards more positive potentials with increasing acid concentrations until, at acid concentrations above 1*M*, the wave was indistinguishable from that due to the anodic dissolution of mercury. At concentrations $\leq$0·01*M*, the efficiency of the extraction decreased to 20% or less. An acid concentration of *ca.* 0·1*M* was selected as being the most suitable and under these conditions the reduction wave occurred at −0·13 V.

Thiocyanate concentration

The reduction wave characteristics were found to be independent of the thiocyanate concentration provided it was between 1 and 4*M*. Low concentrations, $<$*ca.* 0·05*M*, gave incomplete extraction and high concentrations, $>$*ca.* 7*M*, moved the wave to more positive potentials so that it became difficult to distinguish from the anodic wave due to the dissolution of mercury.

The other experimental parameters, *viz.* drop-time, distance between electrodes, mercury pressure, supporting electrolytes and deoxygenation were as found in the previous communication.[1]

GENERAL METHOD

Reagents

Standard $10^{-3}M$ ammonium molybdate solution was prepared by dissolving 0·1766 g of analytical grade ammonium molybdate $[(NH_4)_6Mo_7O_{24}.4H_2O]$ in distilled water and diluting to 1 l. Other reagents were as described under *Preliminary polarographic investigation.*

Procedure

Add 2·5–15 ml of $10^{-3}M$ molybdenum solution to a 100 ml separating funnel, followed by 2·5 ml of 1*M* hydrochloric acid, 1–2 g of ascorbic acid and 5 ml of saturated ammonium thiocyanate solution. Dilute to *ca.* 25 ml with distilled water and extract with 15 ml of diethyl ether. Transfer the organic phase to a 25 ml volumetric flask, add 5 ml of 0·5*M* lithium chloride in methanol and dilute to volume with methanol. Deoxygenate an aliquot (5 ml) of this solution with a fast stream of oxygen-free nitrogen for 2 min and polarograph it from zero to −0·5 V *vs.* mercury pool with an instrument sensitivity of 5 μA/full scale deflection. Measure the height of the wave of $E_{\frac{1}{2}}$ −0·13 V.

A graph of wave-height against concentration of molybdenum is a straight line from 10–60 ppm, which is a suitable working range for the procedure given. The relative standard deviation from the analysis of nine solutions, each $4 \times 10^{-4}M$ in molybdenum, was 2·3%.

Extractions have been carried out from 500 ml of aqueous phase (pre-saturated with diethyl ether) containing the same amounts of molybdenum as used for the calibration curve. An exactly similar calibration curve was obtained and the overall sensitivity was increased to cover the range 0·5–3·0 ppm.

Interferences

The effect of those ions listed in Table I, together with Cd(II) and Cr(VI), was determined. The tests were carried out with a 10-fold molar excess of these ions in a solution $4 \times 10^{-4}M$ in molybdenum(V) taken through the recommended extraction procedure. The height and position of the reduction wave was not altered by any of these ions. The aqueous phase was also made 0·1*M* in hydrochloric, nitric, sulphuric and perchloric acids. Again, no difference was noted.

TABLE I.—HALF-WAVE POTENTIALS OF SOME METAL THIOCYANATE COMPLEXES

Metal ion	Aqueous phase	Aqueous phase plus SCN^-	Aqueous phase after extraction	Organic phase
	−1·35* (CHW)†	−0·90 (CHW)†	−0·90 (CHW)†	−1·0 (CHW)†
As(III)	−0·50, −0·74	−0·42, −0·70	−0·42, −0·70	—
Be(II)	—	—	—	—
Bi(III)	−0·14	−0·04	−0·04	—
Co(II)	−1·28	—	—	—
Cu(I)	−0·25	−0·38	−0·38	—
Cu(II)	−0·24	>0·0, −0·42	>0·0, −0·42	—
Fe(II)	—	—	—	—
Fe(III)	>0·0	>0·0	—	>0·0
Ga(III)	—	−0·80	—	—
In(III)	−0·64	−0·68	—	—
Mo(V)	*ca.* −0·28, −0·51, −0·82	>0·0	—	−0·09
Mo(VI)	−0·24, −0·75	>0·0	—	−0·10
Ni(II)	−0·98	—	—	—
Pd(II)	>0·0	>0·0	>0·0	—
Sb(III)	−0·18	>0·0	>0·0	—
Sc(III)	—	—	—	—
Sn(II)	−0·52	−0·50	−0·50	—
Sn(IV)	−0·18, −0·54	−0·36	—	—
Ti(IV)	−0·86	−0·16	−0·16	—
U(VI)	−0·25	>0·0	>0·0	—
V(V)	>0·0, −1·03	>0·0, −0·46	>0·0, −0·46	—
W(VI)	—	—	—	—
Zn(II)	−1·02	—	—	—

* Potential *vs.* mercury pool electrode, in volts.
† CHW denotes catalytic hydrogen wave.

Analysis of steel

In view of the great selectivity obtained by the combination of solvent extraction and polarography, it was decided to try the method for the determination of molybdenum in mild and alloy steels.

Procedure

Dissolve a suitable weight (0·1–1 g) of the steel, containing not less than 250 μg of molybdenum in 10 ml of concentrated hydrochloric acid in a 100-ml beaker, warming to assist dissolution. Evaporate the solution almost to dryness (avoid baking) and re-dissolve the residue in 10 ml of 0·5*M* hydrochloric acid. If a large amount of tungsten is present, add sufficient citric acid solution to obtain complete dissolution. Transfer the solution to a 250-ml separating funnel and dilute to *ca.* 40 ml. Add 1–2 g of ascorbic acid and 10 ml of aqueous saturated ammonium thiocyanate solution, and finish as described above under *General procedure*.

TABLE II.—DETERMINATION OF MOLYBDENUM IN B.C.S. STEELS

Sample No.	Type of steel	Found, %	Certified value, %	Spread in certificate values, %
273	mild steel	0·045 0·041 0·040	$0{\cdot}04_5$	0·041–0·046
275	mild steel	0·100 0·101	$0{\cdot}09_5$	0·092–0·100
320	mild steel	0·208 0·217	0·22	0·21–0·22
321	mild steel	0·069 0·068 0·065	0·068	0·064–0·072
323	mild steel	0·105 0·104 0·111	0·100	0·095–0·105
325	mild steel	0·167 0·167	0·16	0·15–0·16
219/2	alloy steel	0·421 0·439	0·43	0·40–0·45
241/1	alloy steel	0·511 0·516	0·52	0·51–0·52

A calibration curve obtained by taking 1 g of electrolytic iron with standard molybdenum aliquots through the procedure was the same as the one obtained without iron present.

The results of the analysis of some British Chemical Standards mild and alloy steels are shown in Table II.

Résumé—Une technique comportant l'extraction par solvant du thiocyanate de molybdène (V) en éther-diéthylique suivie d'un examen polarographique direct de la phase organique offre une méthode sélective de dosage du molybdène jusqu'à 0,5 ppm. Parmi les 21 éléments examinés, on a observé que seul le molybdène donne une vague de réduction dans les conditions recommandées. On évalue la méthode en ce qui concerne divers facteurs expérimentaux et l'applique au dosage du molybdène dans l'acier doux et les alliages d'acier.

Zusammenfassung—Ein Verfahren, bei dem Molybdän (V)-rhodanid in Diäthyläther extrahiert und die organische Phase dann direkt polarographisch untersucht wird, bietet eine selektive Methode zur Bestimmung von Molybdän bis herunter zu 0,5 ppm. Unter 21 untersuchten Elementen gibt nur Molybdän unter den empfohlenen Bedingungen eine Reduktionsstufe. Die Methode wird bezüglich mehrerer experimenteller Variabler optimiert und auf die Bestimmung von Molybdän in kohlenstoffarmen und legierten Stählen angewandt.

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DETERMINATION OF LOW CONCENTRATIONS OF HYDROGEN HALIDES AND HALOGENS IN THE GAS PHASE

REMOVAL FROM A MIXTURE OF GASES AND QUANTITATIVE ESTIMATION

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Summary—A method has been developed for the removal of hydrogen chloride, and mixtures of bromine and hydrogen bromide, from gaseous mixtures by absorption on various solids. The efficiency of removal of bromine and hydrogen bromide has been determined and the substances have been estimated potentiometrically. The technique is extended to include the other halogens and hydrogen halides.

SMALL quantities of hydrogen halides or halogens (~0·3 mole %) are often produced in gaseous reactions (for example in the decomposition of hot radicals produced by the flash photolysis of halomethanes[1]) or used as traps for organic free radicals.[2] Halogens may be estimated spectrophotometrically,[2,3] but this is not feasible for hydrogen halides. It is sometimes necessary to remove these substances from a gaseous reaction mixture prior to condensing the products and reactants in a liquid-nitrogen trap. Acetone, for example, reacts in the presence of hydrogen halides in the condensed phase to give polymers.[2]

The present work is concerned primarily with a method for the efficient removal of hydrogen chloride and mixtures of bromine and hydrogen bromide and secondarily with their quantitative estimation. These compounds are being used as radical traps in organic free radical studies.[4] The technique is extended to include methods for the isolation and estimation of the other halogens and hydrogen halides.

EXPERIMENTAL

Absorption efficiency

Hydrogen chloride, hydrogen bromide (Matheson), and carbon dioxide (prepared from crushed solid) were dried by passage through "drierite" (B.D.H.) and purified by bulb-to-bulb distillation. Bromine (May & Baker) was thoroughly degassed and similarly purified. The auramine (B.D.H.) used contained some of the hydrochloride which was reduced to a low level by repeated extraction with ethanol in a Soxhlet extractor, followed by recrystallization (five times) from ethanol. 1-Amino-anthraquinone (Hopkins & Williams) was used as received. All the other absorbents were obtained from B.D.H. The apparatus has been described in detail elsewhere.[5]

Various mixtures of carbon dioxide, hydrogen bromide and bromine, or carbon dioxide and hydrogen chloride, were expanded from a 300-ml cylindrical vessel through an absorption trap (Fig. 1) and any residual gas was removed by an automatic Töpler pump and measured in the gas burette. This provided a method for estimating the efficiencies of the various absorbents for removing hydrogen chloride, hydrogen bromode or bromine. The absorbents used are listed in Table I or referred to in the discussion.

Potentiometric titration of halide

A method used in this department was adapted to the micro-scale. The titration cell consisted of a wide-necked conical flask in which the solution was stirred magnetically. The cathode was a length

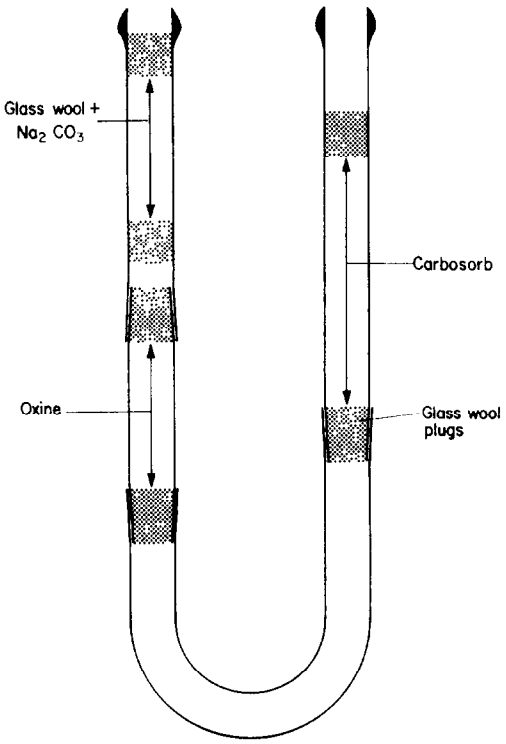

FIG. 1.—The absorption trap.

TABLE I.—EFFICIENCY OF ABSORPTION OF GASES ON VARIOUS SOLIDS

Solid	Gas	Colour change or effect on solid	Efficiency of absorption %	Remarks
	HBr	orange	100	
	Br_2	black	100	
Auramine	MeBr	—	5	non-selective
(yellow)	t-BuOBr	green	100	
	HCl	orange	100	
	HBr		20	
	Br_2		20	
Glycine	HI		100	ref. 6.
	HCl		100	
8-Hydroxy-quinoline	HBr		$0 \pm 0{\cdot}2$	selective for Br_2
	Br_2		100	
1-Naphthylamine	HBr	liquefies	100	non-selective
	Br_2		100	
Potassium carbonate	HBr	yellow	100	Br_2 may be washed out by using iso-butanol.
	Br_2		a little	
Sodium carbonate	HBr		100 ± 6	
	HCl		100 ± 1	
	Br_2		v. little	
Sodium bicarbonate	HBr		100	ref. 7.

of silver wire, 2 mm in diameter, surrounded by a 1-cm diameter plastic tube pierced with several 3-mm diameter holes. The anode was a platinum wire sealed into the capillary tip of an Agla micrometer syringe. The tip dipped into the halide solution to complete the cell $(Ag/Ag^{+}(a_1)\|Ag^{+}(a_2)/Ag/Pt)$. The initial voltage of the cell depends on the silver nitrate concentrations but was usually ~400 mV. The voltage was measured on a Tinsley potentiometer (type 3184D) *via* a simple electrometer (Fig. 2) based on a Mullard ME1400 valve enclosed in an airtight box dried with silica gel. The L.T. supply was 4·4 V and the H.T. supply was 45 V. The arrangement is a little unusual in that the cell produces reverse bias on the control grid. The electrometer was checked for linearity with a Mullard dual-beam oscilloscope. The output voltage was adjusted to 1400 mV and 10 ml of ethanol were added to the halide solution at the beginning of each titration to improve the end-point.

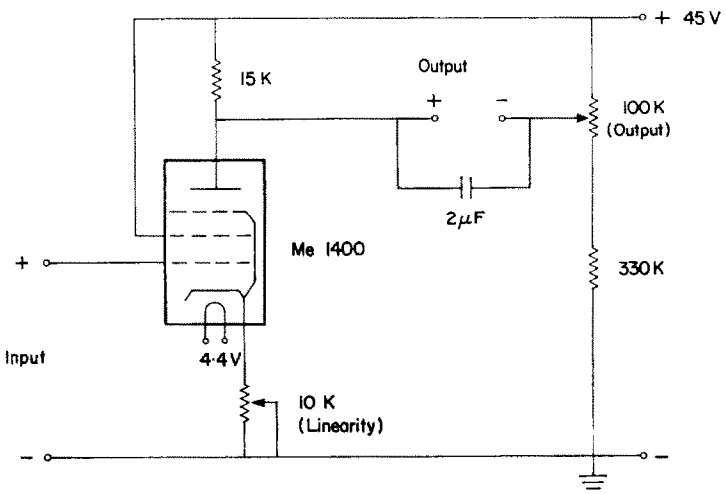

FIG. 2.—Circuit for the potentiometric titration.

Preparation of sample for titration

With auramine (for HX only). A column of purified auramine 2·5 cm long and 1 cm diameter was sufficient to absorb several mmoles of halide. The auramine was pushed out of the U-tube and any residue washed out with 10 ml of acetone, followed by 20 ml of de-ionized water, and was then hydrolysed by addition of 1 pellet of sodium hydroxide and boiling for 12 hr. This resulted in the production of ammonia and Michler's ketone, the solution changing from yellow to almost colourless. The cooled mixture was washed with four 50 ml portions of benzene, which removed most of the ketone. The colourless aqueous solution was made acid to litmus by addition of dilute nitric acid and titrated with 0·05*M* silver nitrate.

With sodium carbonate–oxine–soda-lime (for hydrogen chloride or hydrogen bromide–bromine mixtures). The surface area of the sodium carbonate in the column (8 cm long and 1 cm diameter) was increased by mixing it with glass wool, which minimized the amount of sodium carbonate used. This column was followed by a column of soda-lime 2·5 cm long and 1 cm diameter which had been degassed thoroughly by being kept at 80° under vacuum for 2 hr. The columns (see Fig. 1) were separated from each other by glass wool and connected by ground glass joints. During a run, the entire U-tube was maintained at 80° by placing it in a water-bath. The columns in the order stated, removed hydrogen bromide, bromine and carbon dioxide respectively. The sodium carbonate was dissolved in enough dilute nitric acid to give a solution just acid to litmus, 10 ml of ethanol were added and the halide was titrated.

DISCUSSION

Table I summarizes the results for the isolation of hydrogen chloride, hydrogen bromide or hydrogen bromide + bromide by absorption on various solids. Anthraquinone, phenanthrene, fluorescein and calcium carbonate were useless as absorbents. Copper, magnesium, naphthalene and 1-amino-anthraquinone absorbed only small amounts of gas.

By far the most efficient absorbent was auramine,[2] but it is not selective in its absorption properties, being equally efficient for hydrogen bromide, bromine and t-butyl hypobromite.[4] The mechanism for the absorption of HX is presumably *via* salt formation. There are three possible positions where this may occur in the auramine molecule and probably all three are involved. This would explain the high efficiency of auramine. The absorption efficiency increases if the temperature is raised to 80°. In addition to indiscriminate absorption of hydrogen bromide and bromine, auramine had the disadvantage that it was impossible to estimate the absorbed halide because of erratic cell voltages caused by organic compounds in the solution. Michler's

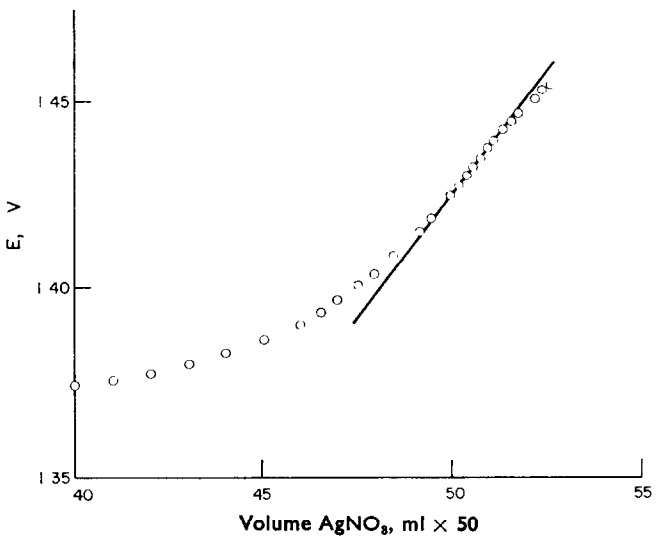

FIG. 3.—Typical curve for potentiometric titration of halide.

ketone is slightly soluble in water, and its presence is shown by the production of a yellow colour on acidification. Addition of Nonex 501 minimized the variation in cell voltage.

The sodium carbonate–oxine system was much more convenient because the carbonate selectively absorbed hydrogen bromide, gave a blank titre of only 0·2 μmole of halide and provided accurate, reproducible titrations. Accuracy was checked by the estimation of weighed, dried samples ($\sim$60 μmole) of analytical reagent grade potassium bromide and potassium chloride (B.D.H.) Smooth titration curves were obtained (Fig. 3) of which the point of inflection was taken as the end-point. Differential plots were unsatisfactory, but the end-point was readily found as the mid-point of the steepest slope.

The hydrogen chloride from hydrogen chloride–carbon dioxide mixtures (1:8) was determined by the potentiometric method to better than 1%. When hydrogen chloride or hydrogen bromide reacts with sodium carbonate, about 30% of their volume of carbon dioxide is produced and with large amounts of them, water can be detected. With gaseous mixtures of hydrogen bromide and bromine, diluted with carbon dioxide (1:8), analysis of hydrogen bromide was reproducible within $\pm$6% but it was impossible to estimate bromine. Oxine, although a selective absorbent for

bromine, was subject to the same analytical difficulties as auramine. Direct weighing proved unsuccessful because of the relatively high vapour pressure of the oxine and consequent loss by sublimation. A large scale oxygen flask determination of the bromine might be successful. Since the mixture passes through the sodium carbonate first, the bromine probably interferes with the hydrogen bromide analysis *via* the equilibrium

$$Br_2 + H_2O \rightleftarrows HBr + HOBr,$$

and hence accounts for the 6% error. The carbon dioxide produced was removed with 100% efficiency by soda-lime.

Thus small amounts of hydrogen chloride, hydrogen bromide and hydrogen iodide may be absorbed efficiently on columns of sodium carbonate backed by a column of soda-lime, and estimated within 1%. Tests with hydrogen fluoride have not been carried out although a solution of hydrogen fluoride produces the same colour with auramine, so that there is every indication that auramine will also be effective for hydrogen fluoride. Mixtures of hydrogen bromide and bromine can be selectively absorbed on columns of sodium carbonate, oxine and soda-lime used in that order. It should be possible to adapt this system for other halogen/hydrogen halide mixtures, the halogens being estimated spectrophotometrically as indicated earlier. It has been shown that fluorine reacts quantitatively with calcium oxide, the liberated oxygen giving a quantitative measure of the fluorine absorbed.[8]

Acknowledgements—The authors are indebted to Dr. B. Chamberlain (Pilkington Bros., Latham, Lancs) for helpful discussions about the potentiometric titration set-up. One of us (F.R.C.) gratefully acknowledges the receipt of a Carnegie Scholarship from the Carnegie Trust for the Universities of Scotland.

Zusammenfassung—Es wurde eine Methode entwickelt zur Entfernung von Chlorwasserstoff und Mischungen von Brom und Bromwasserstoff aus Gasgemischen durch Adsorption an verschiedenen Festkorpern. Der Wirkungsgrad der Entfernung von Brom und Bromwasserstoff wurde ermittelt und die Substanzen potentiometrisch bestimmt. Das Verfahren wird auf die anderen Halogene und Halogenwasserstoffe ausgedehnt.

Résumé—On a élaboré une méthode pour éliminer l'acide chlorhydrique et des mélanges de brome et d'acide bromhydrique de mélanges gazeux par adsorption sur divers solides. On a déterminé le pouvoir d'élimination pour le brome et l'acide bromhydrique et estimé potentiométriquement ces substances. On a étendu la technique pour y inclure les autres halogènes et acides halogènhydriques.

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POLAROGRAPHY OF LEAD ITACONATE COMPLEXES

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Summary—The complexation of lead ions with itaconic acid (H_2A) has been studied polarographically at 30°. At $pH < pK_1$, the complex species $Pb(HA)^+$ was identified. At $pK_1 < pH < pK_2$ and $pH > pK_2$ the formation of Pb(A) and $Pb(A)_2^{2-}$ respectively, was confirmed. The dissociation constant of $Pb(A)_2^{2-}$ was found to be $8{\cdot}3 \times 10^{-5}$. The electrode reactions were established.

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THE polarographic behaviour of the complexes of lead with formic acid and tartaric acid has been studied by Hershenson *et al.*,[1] and Iwase,[2] respectively. The complexes of lead with glutamic acid,[3] glycollic acid and malonic acid[4] have been investigated polarographically.

Although the polarography of the uranyl itaconate system has been investigated,[5] the lead itaconate system has not been studied previously. This work was undertaken to present a complete picture of the polarographic behaviour of this system.

EXPERIMENTAL

Apparatus

All polarograms were obtained with a Fisher Elecdropode. The applied potential was measured accurately with Leeds and Northrup Student Potentiometer. A modified H-type cell, containing a saturated calomel reference electrode separated from the solution compartment by a fine sintered-glass disk and a potassium chloride–agar plug, was used. The cell was immersed in a water thermostat at 30° ± 0·01°. Dissolved oxygen was displaced from the polarographic solutions by hydrogen, which was scrubbed by passage through an alkaline solution of sodium pyrogallate. The capillary characteristics of the dropping mercury electrode were: $m = 1{\cdot}685$ mg/sec and $t = 4{\cdot}53$ sec/drop at 71·4 cm height of mercury in 0·3*M* potassium nitrate solution at an applied potential of −0·45 V.

The pH was adjusted with nitric acid or carbonate-free potassium hydroxide solution, and measured with a Toa Electronics HM-5A pH meter.

Chemicals

The stock solution of 0·01*M* lead nitrate was standardized complexometrically with standard EDTA solution.[6] The itaconic acid was of c.p. grade and its solution was standardized against carbonate-free sodium hydroxide solution which had itself been standardized with potassium hydrogen phthalate from the National Bureau of Standards.

Potassium nitrate solution was used as supporting electrolyte. A maximum suppressor was not used, as no maxima were observed.

RESULTS AND DISCUSSION

Nature of the reduction

As can be observed from Fig. 1, the half-wave potential of the simple lead ion in 0·3*M* potassium nitrate solution at pH 3·20 is −0·396V *vs.* S.C.E.; the half-wave potentials are all shifted to more negative values by the complexation of lead ion with itaconic acid, and by the variation in pH value, showing that hydrogen ion is involved in the electrode reduction of the complex.

The polarographic characteristics of the lead itaconate complexes were studied systematically over the pH range 1·65–7·70 by polarographing a solution of 1·055 ×

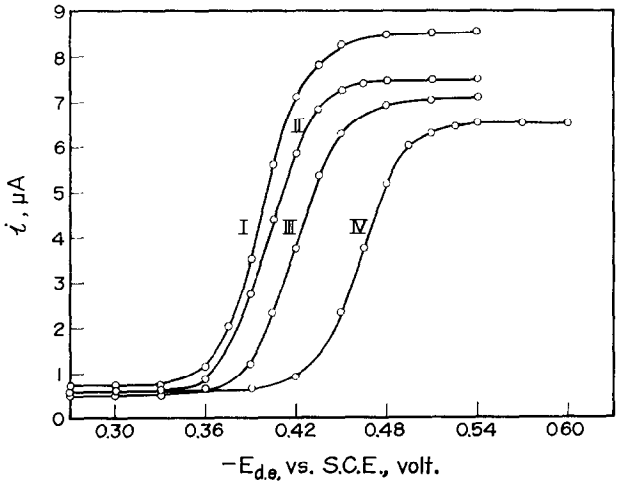

FIG. 1.—Typical polarograms.
I. $1{\cdot}055 \times 10^{-3}M$ $Pb(NO_3)_2$, $0{\cdot}3M$ KNO_3 at pH 3·20
II. plus $0{\cdot}1M$ itaconic acid at pH 3·52
III. plus $0{\cdot}3M$ itaconic acid at pH 3·25
IV. plus $0{\cdot}3M$ itaconic acid at pH 4·80.

$10^{-3}M$ lead nitrate in $0{\cdot}3M$ itaconic acid and $0{\cdot}3M$ potassium nitrate. The upper limit of pH in these measurements is restricted by the precipitation of lead ion. As shown in Table I, both the mean value of $E_{3/4} - E_{1/4}$ and the mean slope of the conventional logarithmic plots were −0·031V *vs.* S.C.E. These are in excellent agreement with the theoretical value for a reversible two-electron reduction.

The temperature coefficient of the half-wave potential is −0·63 mV/deg in the temperature range 25–40°, giving further evidence of the reversible character of the reduction. The temperature coefficient of the diffusion current is 0·16%/deg, and the value of $i_d/h^{1/2} = 0{\cdot}790 \pm 0{\cdot}037$ for the height of mercury column from 35·67 to 83·30 cm. These data demonstrated that the electrode reductions were entirely diffusion controlled processes.

Effect of pH on the half-wave potential

The dependence of half-wave potential on the pH value for solutions of $1{\cdot}055 \times 10^{-3}M$ lead nitrate in $0{\cdot}3M$ potassium nitrate and varying concentrations of itaconic acid from $0{\cdot}05M$ to $0{\cdot}80M$ is shown in Fig. 2. When the pH value is lower than 2·3, the half-wave potentials kept a constant value at −0·396V *vs.* S.C.E., which is identical with the half-wave potential of the simple lead ion. This indicates that lead does not form complexes with itaconic acid below pH 2·3. At pH values between 2·3 and 5·7, the half-wave potentials are shifted to more negative values as the pH is increased. The slopes of the straight lines increase with increasing concentration of ligand and a mean value of −0·029 was obtained for ligand concentrations between 0·3 and $0{\cdot}8M$. This shows that one hydrogen ion is involved in the electrode reduction. When the pH value is increased to higher than 5·7, which corresponds to the pK_2 of the itaconic acid,[7] the half-wave potential becomes independent of pH indicating that no hydrogen ion is involved in the reduction.

TABLE I.—POLAROGRAPHIC CHARACTERISTICS AND REVERSIBILITY

pH	$E_{1/2}$ *vs.* S.C.E. *V*	$E_{3/4} - E_{1/4}$	Slope, $E_{d.e}$ *vs.* $\log\left(\frac{i}{i_d - i}\right)$	i_d, μA
1·65	−0·396	−0·032	−0·032	7·11
2·02	−0·396	−0·030	−0·031	6·72
2·27	−0·396	−0·033	−0·032	6·71
2·50	−0·403	−0·031	−0·030	6·63
2·62	−0·404	−0·033	−0·032	6·34
2·75	−0·405	−0·031	−0·031	6·15
2·93	−0·414	−0·030	−0·031	6·45
2·95	−0·417	−0·029	−0·030	6·51
3·10	−0·417	−0·028	−0·029	6·15
3·25	−0·420	−0·030	−0·030	6·45
3·35	−0·424	−0·031	−0·030	6·20
3·60	−0·429	−0·033	−0·032	6·35
3·95	−0·437	−0·033	−0·032	6·00
4·10	−0·443	−0·033	−0·033	6·15
4·20	−0·446	−0·033	−0·032	6·15
4·40	−0·450	−0·030	−0·031	5·55
4·45	−0·456	−0·033	−0·033	6·05
4·80	−0·464	−0·032	−0·031	5·75
5·00	−0·468	−0·033	−0·032	6·05
5·43	−0·478	−0·033	−0·032	5·55
5·60	−0·477	−0·030	−0·031	5·30
5·80	−0·480	−0·031	−0·030	5·72
6·35	−0·483	−0·031	−0·031	5·70
6·60	−0·483	−0·032	−0·031	5·87
6·90	−0·483	−0·029	−0·029	5·78
7·20	−0·483	−0·029	−0·030	5·35
7·70	−0·483	−0·029	−0·029	5·40

($1{\cdot}055 \times 10^{-3}M$ lead nitrate, $0{\cdot}3M$ itaconic acid and $0{\cdot}3M$ potassium nitrate).

Complex species and the half-wave potential

Itaconic acid is an unsaturated dicarboxylic acid with $pK_1 = 3{\cdot}8$ and $pK_2 = 5{\cdot}7$.[7] Since the probable ligand in the lead itaconate complex in acid solution may be either the protonated itaconate ion (HA^-) or the itaconate ion (A^{2-}), a generalized equation for the half-cell reaction of the complexes can be expressed as

$$Pb(HA)_p^{2-p} + 2e + Hg = Pb(Hg) + pHA^- \quad (1)$$

or

$$Pb(A)_p^{2-2p} + 2e + Hg = Pb(Hg) + pA^{2-}. \quad (2)$$

The half-wave potentials of equations (1) and (2) can be expressed as

$$(E_{1/2})_c = (E_{1/2})_s + \frac{0{\cdot}060}{2}\log K - \frac{0{\cdot}060}{2}\,p\log C_{H_2A} - \frac{0{\cdot}060}{2}p\log K_1 - \frac{0{\cdot}060}{2}p\log [H^+] + \frac{0{\cdot}060}{2}p\log ([H^+]^2 + K_1[H^+] + K_1K_2) \quad (3)$$

and

$$(E_{1/2})_c = (E_{1/2})_s + \frac{0{\cdot}060}{2}\log K - \frac{0{\cdot}060}{2}p\log C_{H_2A} - \frac{0{\cdot}060}{2}p\log K_1K_2 + \frac{0{\cdot}060}{2}p\log ([H^+]^2 + K_1[H^+] + K_1K_2) \quad (4)$$

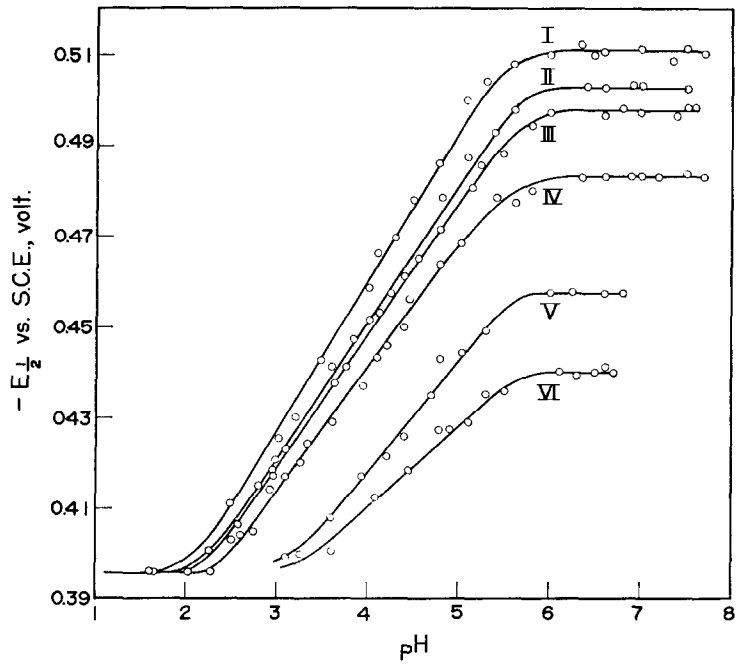

FIG. 2.—Effect of pH on the half-wave potential
$1{\cdot}055 \times 10^{-3}M$ $Pb(NO_3)_2$, $0{\cdot}3M$ KNO_3, and
I. $0{\cdot}8M$ itaconic acid IV. $0{\cdot}3M$ itaconic acid
II. $0{\cdot}6M$ itaconic acid V. $0{\cdot}1M$ itaconic acid
III. $0{\cdot}5M$ itaconic acid VI. $0{\cdot}05M$ itaconic acid.

respectively, where K is the dissociation constant of the complex, and C_{H_2A} is the analytical concentration of itaconic acid.

We may distinguish three cases according to the pH value of the solution: (*a*) $pH < pK_1$, (*b*) $pK_1 < pH < pK_2$, and (*c*) $pH > pK_2$. In these cases equation (3) simplifies to

$$(a) \qquad (E_{1/2})_c = \text{const.} - 0{\cdot}030\, p \log C_{H_2A} - 0{\cdot}030\, p\ pH \qquad (5)$$

$$(b) \qquad (E_{1/2})_c = \text{const.} - 0{\cdot}030\, p \log C_{H_2A} \qquad (6)$$

$$(c) \qquad (E_{1/2})_c = \text{const.} - 0{\cdot}030\, p \log C_{H_2A} + 0{\cdot}030\, p\ pH. \qquad (7)$$

And for the same three pH conditions equation (4) simplifies to

$$(a)' \qquad (E_{1/2})_c = \text{const.} - 0{\cdot}030\, p \log C_{H_2A} - 0{\cdot}060\, p\ pH \qquad (8)$$

$$(b)' \qquad (E_{1/2})_c = \text{const.} - 0{\cdot}030\, p \log C_{H_2A} - 0{\cdot}030\, p\ pH \qquad (9)$$

$$(c)' \qquad (E_{1/2})_c = \text{const.} - 0{\cdot}030\, p \log C_{H_2A}. \qquad (10)$$

These equations demonstrate that if the ligand is protonated, the slopes of the straight lines for the plots of $(E_{1/2})_c$ *vs.* pH are $-0{\cdot}030p$, zero and $+0{\cdot}030p$ respectively, for the three pH conditions of (*a*), (*b*) and (*c*), whereas if the ligand is deprotonated, the slopes are $-0{\cdot}060\,p$, $-0{\cdot}030\,p$ and zero.

It is obvious from Fig. 2 that the plots of $(E_{1/2})_c$ *vs.* pH break at pH 5·7 ($= pK_2$) and the mean slope of the straight lines is $-0{\cdot}029$ up to the pH value 5·7. When the pH value is greater than 5·7, the slope is zero.

Equations (5) and (9) show that the plots of $(E_{1/2})_c$ *vs.* pH have the same slope of $-0{\cdot}030\ p$. This behaviour can be correlated with the fact that there was no break point observed at pH 3·8 (= pK_1) in Fig. 2, and provides evidence that the ligand species is HA^- at pH $<$ pK_1 and is A^{2-} at pK_1 < pH < pK_2.

Therefore, it was concluded that for condition (*a*), pH < pK_1, the complex species must be $Pb(HA)_p^{2-p}$, corresponding to equation (5) in which $p = 1$; for (*b*), pK_1 < pH < pK_2, the complex species must be $Pb(A)_p^{2-2p}$, corresponding to equation (9) in which $p = 1$; and for (*c*), pH > pK_2, the complex species must be $Pb(A)_p^{2-2p}$, corresponding to equation (10) in which $p = 2$ (as will be shown in the next section).

Effect of ligand concentration on the half-wave potential

The co-ordination number in lead itaconate complexes was determined by a plot of half-wave potential *vs.* logarithm of ligand concentration as shown in Fig. 3. At pH < 5·7 the mean reciprocal slope of the straight lines is 0·036, corresponding to a metal–ligand ratio of 1:1. This result agreed completely with that of the section mentioned above. On the other hand at pH > 5·7, the mean reciprocal slope is 0·061, yielding the metal–ligand ratio 1:2.

Basing on the foregoing data and discussion, the complex species and electrode reactions can be formulated as

$$Pb(HA)^+ + H^+ + 2e + Hg = Pb(Hg) + H_2A \qquad pH < pK_1$$
$$Pb(A) + H^+ + 2e + Hg = Pb(Hg) + HA^- \qquad pK_1 < pH < pK_2$$
$$Pb(A)_2^{2-} + 2e + Hg = Pb(Hg) + 2A^{2-} \qquad pH > pK_2.$$

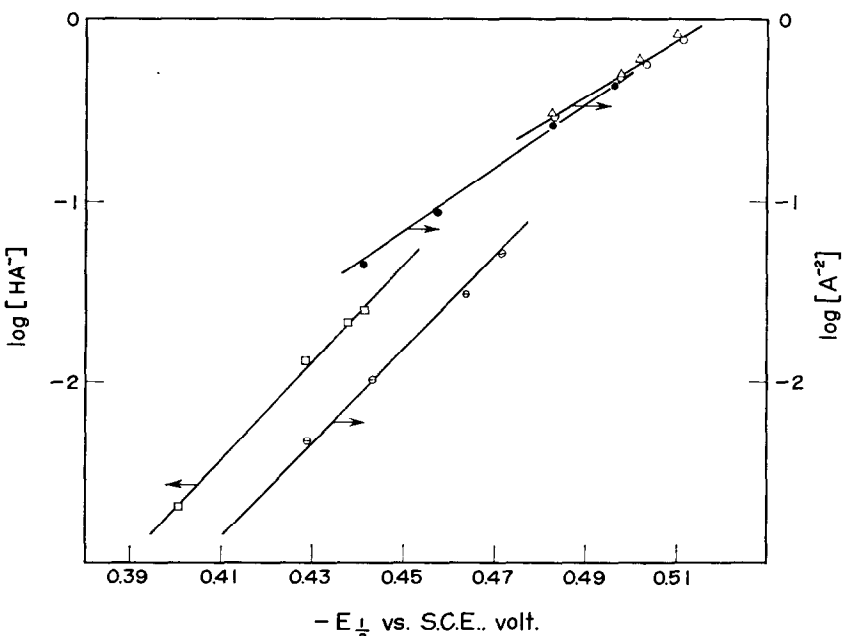

FIG. 3.—Variation of half-wave potential with ligand concentration.
□ pH 3·60 ○ pH 7·00
⊖ pH 4·80 △ pH 7·50
● pH 6·60

Dissociation constant of complex

As shown in Fig. 3, when the pH value is greater than pK_2, the complexes have an almost constant co-ordination number of 1·96, 2·17 and 2·17 at pH 6·60, 7·00 and 7·50, respectively. Applying equation (4) and $(E_{1/2})_s = -0{\cdot}396$V *vs.* S.C.E. (curve I in Fig. 1), the concentration dissociation constant of $Pb(A)_2^{2-}$ was found to be $8{\cdot}3 \times 10^{-5}$ mole^1 l.$^{-2}$ (see Table II).

TABLE II.—DISSOCIATION CONSTANTS OF $Pb(A)_2^{2-}$

pH	C_{H_2A}, M	$(E_{1/2})_c - (E_{1/2})_s$	pK
6·60	0·05	−0·0450	4·151
	0·10	−0·0615	4·111
	0·30	−0·0870	4·026
	0·50	−0·0996	4·011
	0·60	−0·1065	4·086
	0·80	−0·1140	4·091
		mean value	4·079
7·00	0·30	−0·0870	4·081
	0·50	−0·1015	4·082
	0·60	−0·1070	4·094
	0·80	−0·1150	4·090
		mean value	4·087
7·50	0·30	−0·0870	4·052
	0·50	−0·1020	4·070
	0·60	−0·1065	4·048
	0·80	−0·1155	4·077
		mean value	4·062

Acknowledgement—The authors wish to thank the National Council of Science Development for its financial support of this work.

Zusammenfassung—Die Komplexbildug von Bleiionen mit Itaconsäure (H_2A) wurde bei 30° polarographisch untersucht. Bei pH < pK_1 wurde die Komplexspezies $Pb(HA)^+$ identifiziert. Bei pK_1 < pH < pK_2 und pH > pK_2 wurde die Bildung von Pb(A) und $Pb(A)_2^{2-}$ bestätigt. Die Dissoziationskonstante von $Pb(A)_2^{2-}$ wurde zu $8{,}3 \cdot 10^{-5}$ ermittelt. Es wurde festgestellt, welche Elektrodenreaktionen ablaufen.

Résumé—On a étudié la complexation des ions plomb par l'acide itaconique (H_2A) par polarographie à 30°. A pH < pK_1, on a identifié l'espèce complexe $Pb(HA)^+$. A pK_1 < pH < pK_2 et pH > pK_2, on a confirmé la formation de Pb(A) et $Pb(A)_2^{2-}$ respectivement. On a trouvé pour $Pb(A)_2^{2-}$ la constante de dissociation $8{,}3 \times 10^{-5}$. On a établi les réactions à l'électrode.

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FREE RADICAL OXIDATION OF DIHYDRIC PHENOLS WITH DIPHENYLPICRYLHYDRAZYL

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Summary—A spectrophotometric study has been made of the reactions between the free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) and the three dihydric phenols. It has been shown that water affects the rate of all three reactions and the stoichiometry of the DPPH-catechol (pyrocatechol) reaction. Because of the differences in the rate of oxidation in absolute ethanol, it is possible to determine selectively either hydroquinone or catechol in the presence of resorcinol.

THE purple free radical diphenylpicrylhydrazyl (DPPH) has a great potential as an analytical reagent for readily oxidized organic compounds. This has been demonstrated in a limited fashion for mercaptans[1] and phenols[1] and in an elegant fashion for amines[2] and phenols.[3] The phenol-DPPH reaction is kinetically second-order;[3] it has been proposed[4] that a hydrogen atom is abstracted in a slow step from phenols by DPPH (written below as DPPH· to indicate the unpaired electron). The products are a phenoxy radical (ArO·) and yellow diphenylpicrylhydrazine (DPPH:H):

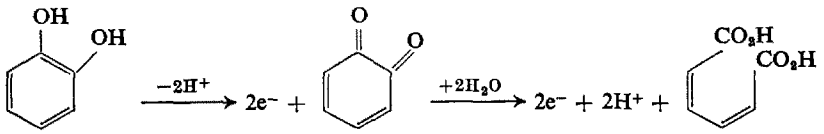
$$\text{DPPH}\cdot + \text{ArOH} \xrightarrow{\text{slow}} \text{DPPH:H} + \text{ArO}\cdot .$$

The analytical technique employed by Blois[1] is based on the measurement of the decrease in absorbance of the 517 mμ peak of DPPH after reaction. The calibration curve is thus a plot of the absorbance of the unchanged DPPH *vs.* the concentration of phenol or mercaptan. In contrast, Papariello and Janish[2,3] plotted the difference (ΔA) between the absorbance values of a DPPH blank and an amine-DPPH mixture *vs.* the amine concentration.

Other workers have studied the kinetics and stoichiometry of DPPH reactions, and many of these papers have been reviewed by Papariello and Janish.[2] In particular, McGowan and Powell[5] have studied the kinetics of certain amine and phenol-DPPH reactions and the effect of certain constituents[6] on phenol-DPPH reactions. Venker and Herzmann[7] found rapid reactions in acetone between DPPH and phenols having at least 2 hydroxyl groups, but no reaction with DPPH and compounds such as resorcinol, phloroglucinol, and phenol. However, Hogg, Lohmann and Russell[4] found that DPPH slowly abstracts an average of 2 hydrogen atoms from monohydric phenols.

The results reported below indicate that water exerts a marked influence on the rate and type of oxidation reaction occurring with catechol (pyrocatechol), hydroquinone and resorcinol. In particular, it appears that catechol and possibly hydroquinone can react with from two to four molecules of DPPH; *i.e.*, undergo 2- or 4-electron oxidations, depending on whether the solvent is anhydrous or not. An

analogy for the 4-electron oxidation of catechol has been reported[8] for the aqueous periodate cleavage of catechol and its ethers:



A 2·7-electron oxidation of hydroquinone by the 2,4,6-tri(t-butyl)phenoxy free radical has also been reported.[9]

EXPERIMENTAL

Apparatus

A transistor-regulated model Bausch and Lomb Spectronic 20 Colorimeter was used for the spectrophotometric measurements. A Beckman model DB spectrophotometer was used in checking the purity of the hydroquinone solutions.

Reagents

2,2-Diphenyl-1-picrylhydrazyl (DPPH) and 1,1-diphenyl-2-picrylhydrazine (DPPH-H) were obtained from Eastman (White Label grade) and were used as received.

Ethanolic solutions of $1 \times 10^{-4}M$ DPPH and $1 \times 10^{-4}M$ DPPH-H were prepared by stirring solvent and solute for 30–45 min. These solutions were then diluted to prepare the reagents used in the study.

Hydroquinone was Eastman White Label grade. Catechol (pyrocatechol) was a Matheson reagent, and resorcinol was Baker and Adamson U.S.P. grade. All $2{\cdot}5 \times 10^{-4}M$ alcoholic phenol solutions were prepared by dilution of a solution of 11·0 mg/100 ml of the appropriate phenol. Whenever absolute ethanol was used as solvent, it was first dried over "Drierite" for at least 24 hr.

Procedure

Time studies of the DPPH-dihydroxyphenol reactions in absolute and 95% ethanol were made by adding 25 ml of $1 \times 10^{-4}M$ DPPH to 2 ml of $2{\cdot}5 \times 10^{-4}M$ solution of the respective phenol, and diluting to 50 ml with the appropriate solvent. (For resorcinol, 5 ml of a $2{\cdot}5 \times 10^{-4}M$ solution were added.) Absorbance readings were taken at 540 mμ at appropriate times, a $5 \times 10^{-5}M$ solution of DPPH-H being used to set 100% transmission. All reaction mixtures were kept in the dark between readings to avoid the slow photochemical reduction of the DPPH to DPPH-H which occurs in sunlight and at 520 mμ.[10]

The amount of 2-electron reaction occurring in the time studies was determined by multiplying the per cent decrease in absorbance by the initial radical concentration and then dividing by twice the molar concentration of the particular phenol.

Linearity of the calibration curves[1] in absolute and 95% ethanol was investigated by adding 25 ml of $1{\cdot}28 \times 10^{-4}M$ DPPH to appropriate aliquots of $2{\cdot}5 \times 10^{-4}M$ solutions of each phenol, diluting to 50 ml with the appropriate solvent, and measuring the absorbance at 540 mμ after about 1 hr of reaction under room lighting.

The interference of resorcinol in the determination of catechol and hydroquinone in absolute ethanol was studied by adding various amounts of $1 \times 10^{-3}M$ resorcinol to 1 ml of $2{\cdot}5 \times 10^{-4}M$ catechol or hydroquinone, then adding the $1 \times 10^{-4}M$ DPPH solution, as in the time studies above. Absorbance readings were taken at 540 mμ after 50 min (catechol) and 140 min (hydroquinone) reaction.

Spectrophotometric measurements were always made at 540 mμ to avoid the interference from DPPH-H encountered at 520 mμ on the Spectronic 20. (The absorption peak is at 517 mμ.)

RESULTS AND DISCUSSION

The relative rates of three selected DPPH-phenol reactions are shown in Fig. 1. It is obvious that the water in 95% ethanol makes the rate of the 2-electron oxidation of catechol to *o*-benzoquinone faster than the rate of this oxidation in absolute ethanol. It is also apparent that water permits reaction between DPPH and resorcinol although Venker and Herzmann[7,11] report that no such reaction occurs in dry acetone.

After a very rapid 2-electron oxidation of catechol, a slower oxidation reaction occurs. The main reaction is presumably the 2-electron oxidation of *o*-benzoquinone to *cis,cis*-muconic acid observed with aqueous periodate by Adler and Magnusson.[8]

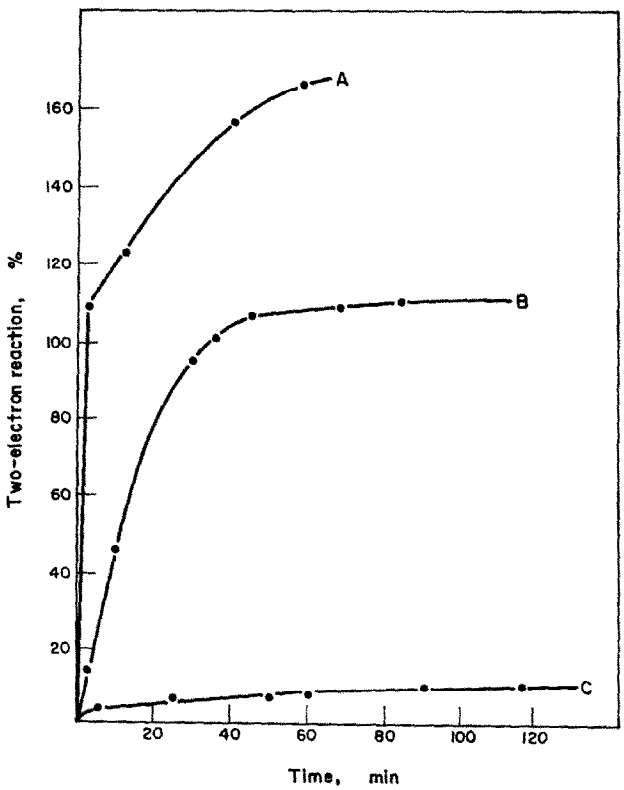


FIG. 1.—Relative rates of DPPH-dihydric phenol reactions.
A 8:1 DPPH:catechol in 95% ethanol
B 5:1 DPPH:catechol in absolute ethanol
C 1:1 DPPH:resorcinol in 95% ethanol.

As indicated in Table I, however, the reaction of DPPH and catechol in 95% ethanol does not terminate at a point corresponding to a 4-electron oxidation, but proceeds well beyond that point. As Adler and Magnusson note, this is probably a side reaction involving an oxidizing agent (DPPH) and decomposition of *o*-benzoquinone. This side-reaction must involve more than two electrons. It is difficult to follow this reaction accurately after the first hour or two because DPPH decomposes with time, and the presence of DPPH-H inhibits this decomposition.[12]

Table I indicates that in absolute ethanol resorcinol reacts at a negligible rate with DPPH, but that hydroquinone and catechol both react with about 2 molecules of DPPH. (The 109% result for catechol may be the result of a trace of water in the absolute ethanol or the result of an impurity in the catechol.) In contrast, resorcinol is readily oxidized by DPPH in the method of Papariello and Janish.[3] Catechol would also be oxidized to *cis,cis*-muconic acid in their procedure. The same would

TABLE I.—RATES OF DIHYDRIC PHENOL-DPPH REACTIONS

Dihydric phenol, *μmole*	Amount of 2-electron reaction with 2.5×10^{-5} μmole of DPPH, % 10	40	60	80	120	140	1200 min
Absolute ethanol as solvent							
Catechol, 0·5	45	102	109	109	—	—	—
Hydroquinone, 0·5	27	58	71	83	97	100	—
Resorcinol, 2·5	0	0	0	—	—	—	7
95% ethanol as solvent							
Catechol, 0·5	119	155	165	170	—	—	~260*
Hydroquinone, 0·5	68	93	97	100	—	—	
Resorcinol, 2·5	3	5	7	8	9	—	

* Measured using 4·0 μmole of DPPH.

be true for the aqueous ethanol procedure of Blois,[1] who apparently studied only the stoichiometry of the DPPH-hydroquinone reaction.

Using Blois's technique, we found that both catechol and hydroquinone in 95% ethanol give straight line calibration curves after 60–80 min reaction time. In absolute ethanol, results from catechol deviate somewhat from Beer's law to give a curved calibration graph; a straight line was found for hydroquinone, however.

TABLE II.—DETERMINATION OF CATECHOL AND HYDROQUINONE IN THE PRESENCE OF RESORCINOL ABSOLUTE ETHANOL SOLVENT, $5 \times 10^{-5}M$ DPPH

Mole ratio of resorcinol to hydroquinone or catechol	Compound determined*†	Present, *M*	Found, *M*
0·4:1	Hydroquinone	2.5×10^{-5}	2.35×10^{-5}
2:1	Hydroquinone	1.5×10^{-5}	1.47×10^{-5}
8:1	Hydroquinone	0.5×10^{-5}	0.51×10^{-5}
8:1	Catechol(pyrocatechol)	0.5×10^{-5}	0.5×10^{-5}
12:1	Catechol(pyrocatechol)	0.5×10^{-5}	0.51×10^{-5}
20:1	Catechol(pyrocatechol)	0.5×10^{-5}	0.52×10^{-5}
32:1	Catechol(pyrocatechol)	0.5×10^{-5}	0.53×10^{-5}

* The ranges of the calibration curves are $0.25–2.5 \times 10^{-5}M$ for hydroquinone† and $0.25–2.5 \times 10^{-5}M$ for catechol.†

† The reaction times are 140 min for hydroquinone and 50 min for catechol.

Because resorcinol reacts at a negligible rate with DPPH in absolute ethanol, we investigated the determination of catechol and hydroquinone in the presence of resorcinol, using DPPH and Blois's technique. The results are shown in Table II. It is possible to determine either of these phenols spectrophotometrically in the presence of much larger molar quantities of resorcinol. This is only possible because of the large difference in their relative rates of reaction with DPPH in absolute ethanol, a difference that is not found in 95% ethanol. This selective determination is not possible using either the aqueous ethanol reagent of Blois or the aqueous methanol reagent of Papariello and Janish because resorcinol would then react at an appreciable rate.

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Zusammenfassung—Die Reaktionen zwischen dem freien Radikal 2,2-Diphenyl-1-pikrylhydrazyl (DPPH) und den drei zweiwertigen Phenolen wurden spektrophotometrisen untersucht. Es wurde gezeigt, daß sich Wasser auf die Geschwindigkeit aller drei Reaktionen und die Stochiometrie der DPPH-Brenzkatechinreaktion auswirkt. Wegen der Unterschiede in der Oxydationsgeschwindigkeit in absolutem Äthanol ist es möglich, wahlweise entweder Hydrochinon oder Brenzkatechin in Gegenwart von Resorcin zu bestimmen.

Résumé—On a effectué une étude spectrophotométrique des réactions entre le radical libre 2,2-diphényl 1-picrylhydrazyle (DPPH) et les trois diphénols. On a montré que l'eau modifie la vitesse des trois réactions et la stoechiométrie de la réaction DPPH-pyrocatéchol. Par suite des différences entre les vitesses d'oxydation en éthanol absolu, il est possible de doser sélectivement l'hydroquinone ou le pyrocatéchol en présence de résorcinol.

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SHORT COMMUNICATIONS

Precise determination of uranium in pure uranium and uranium compounds by constant-current coulomeric titration

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RECENTLY Pszonicki[1] described a procedure for the precise determination of uranium in pure uranium compounds, based on the reduction of uranium(VI) in concentrated hydrochloric acid solution, by means of metallic aluminium in the presence of cadmium ions, to uranium(III) which is oxidized to uranium(IV) by protons on the addition of concentrated phosphoric acid. A weighed amount of solid potassium dichromate, sufficient to oxidize all but a few mg of the uranium(IV), is added and the remaining unoxidized material is titrated with a standard solution of potassium dichromate potentiometrically.

To avoid the use of any standard solutions, the last step of this procedure has been modified by adding a small excess of solid potassium dichromate to the uranium(IV) solution and determining the excess by constant-current coulometry. An additional advantage of this new procedure is that in titrating from higher to lower potential values the potential change at the equivalence point is better defined, changing from about 840 to about 670 mV. It was found also that four evaporations with hydrochloric acid to destroy any nitric acid present in the simple solution as recommended by Pszonicki are not absolutely necessary. Evaporation of the acid used to dissolve the sample, followed by only one further evaporation with hydrochloric acid, is sufficient for satisfactory analytical results to be obtained.

EXPERIMENTAL

Apparatus

pH-Meter: Radiometer, type PHM-22r with platinum electrode type P-101 and saturated calomel electrode type K-101.

Constant-current coulometer: Metrohm, type E211, with generating platinum-platinum electrodes with diaphragm, type EA-224.

Magnetic stirrer: Metrohm, type E 349A, with inert plastic covered stirring bars.

Conical flasks, 1000-ml with normal socket joints NS 29/32 and splash heads.[1]

Reagents

Hydrochloric acid, s.g. 1·19
Nitric acid, s.g. 1·40
Ortho-phosphoric acid, s.g. 1·71
Hydrochloric acid, 1*M*
Cadmium chloride (cryst.) 50% aqueous solution
Iron(III) chloride (cryst.), 25% aqueous solution
Aluminium wire, BDH AnalaR, 0·7 mm diameter
Potassium dichromate, NBS Standard No. 136 b

Water twice distilled from quartz. All reagents are of analytical reagent grade.

Preparation of the samples

Preparation of U_3O_8 *samples.* Ignite the sample for 1 hr at 850–880° and cool in a desiccator. Weigh a sample (5·8–5·9 g) with an accuracy of ±0·01 mg. Transfer the sample carefully to a 1000-ml Erlenmeyer flask with a standard taper neck, using 20–30 ml of 1*M* hydrochloric acid for washing out the weighing bottle and the funnel; add 20 ml of concentrated hydrochloric and 1 ml of concentrated nitric acids, and fit the flask with a splash head.[1] Warm the flask at first gently on a hot-plate, swirling occasionally, until the sample dissolves; then boil the solution without removing the splash head and evaporate it almost to dryness. Next remove the flask from the hot-plate for a short time to allow the contents to cool and suck the condensate from the splash head into the flask. Evaporate the solution again almost to dryness, remove the flask from the heat, add through the splash head 20 ml of concentrated hydrochloric acid and suck it into the flask by cooling. Evaporate again almost to dryness and repeat the addition of hydrochloric acid (30 ml) through the splash

head, dipping the flask into cold water to accelerate the suction so as to give better washing of the walls of the flask.

Preparation of uranium metal, UO_2 *and* UO_3 *samples.* Use the procedure already described,[1] modified as above.

Procedure

Weigh, with an accuracy of ±0·01 mg, an amount of solid potassium dichromate (previously dried at 105° and cooled in a desiccator) 2–3 mg more than the theoretical quantity needed for the oxidation of the sample.

To the sample prepared as described above, add 1 ml of 50% cadmium chloride solution and 0·75 g of aluminium wire cut into pieces about 5 cm long. Put the flask, closed by the splash head, on a hot plate at low heat and warm until the solution turns deep red. Wash the splash head with a few ml of 1*M* hydrochloric acid to suck down the small quantity of green condensate and warm until the aluminium wire is completely dissolved. Remove the flask from the plate and add through the splash head 15 ml of concentrated phosphoric acid followed by a few ml of 1*M* hydrochloric acid. Hydrogen is evolved and the solution turns green. Boil for 1 min to drive off hydrogen, wash the splash head with a few ml of 1*M* hydrochloric acid and cool to room temperature with cold water. Remove the splash head, add 100 ml of 25% iron(III) chloride solution, mix well to dissolve the gelatinous precipitate and dilute with 100 ml of 1*M* hydrochloric acid, mixing well again. Add the weighed potassium dichromate, stir until dissolved and transfer the solution to a 600-ml beaker. Introduce the indicating and generating electrodes and the magnetic stirring bar.

Reduce the excess of potassium dichromate using a current of 10 mA and rapid stirring. The potential of the platinum electrode at the beginning of the titration is about 900 mV *vs.* S.C.E. and remains almost unchanged throughout the whole titration period. As the end-point approaches, titrate at first in intervals of 5 sec and later of 2 sec. At least 3 min is necessary to obtain a constant value of the potential.

For the blank determination, put 20 ml of hydrochloric acid in a 1000-ml conical flask fitted with the splash head, and go through all stages of the analysis; after addition of iron(III) chloride solution and 1*M* hydrochloric acid, add 2–3 mg of potassium dichromate, weighed to ±0·01 mg, and titrate as described above. However, owing to the absence of uranium, dissolution of the aluminium in the blank determination is much slower. It was found that the blank value is mainly due to the iron(II) content of the iron(III) chloride solution; for routine determinations it is sufficient to prepare the blank by mixing 30 ml of conc. hydrochloric acid, 15 ml of syrupy phosphoric acid, 100 ml of iron(III) chloride solution and 100 ml of 1*M* hydrochloric acid, adding 2–3 mg $K_2Cr_2O_7$ weighed to ±0·01 mg, and titrating as described.

All weighings must be reduced to vacuum.

General remarks

(a) After a few titrations the platinum indicating electrode may become poisoned; to regenerate it, oxidize the electrode anodically in a 1*M* sulphuric acid solution for a period of at least 30 min, electrolysing with current from a 6-V battery.

(b) In analysing some samples of U_3O_8 it was not possible to obtain a permanent deep-red colour of uranium(III) at the reduction stage. Before the final dissolution of aluminium, the solution

TABLE I.—ANALYSIS OF U_3O_8 SAMPLES

U_3O_8 % NBS 950a	U_3O_8 % (from UO_3)
99·941	100·014
99·941	100·010
99·939	100·014
99·944	100·015
99·945	100·015
99·942 ± 0·003%	100·014 ± 0·003%

turned from red to brown and green. It was found that amounts of nickel and/or cobalt greater than a total of 10 ppm in the sample are responsible for this. The analytical results obtained are, however, unaffected, as was proved by the analysis of known U_3O_8 samples to which 40 ppm of nickel plus cobalt had been added.

RESULTS

The precision of the method for single determination is better than $\pm 0{\cdot}01\%$. Table I shows the results of analysis of NBS U_3O_8 sample No. 950a (certified value $99{\cdot}94 \pm 0{\cdot}02\%$) and a sample of U_3O_8 obtained by ignition of very pure UO_2.

The value obtained for the NBS 950a standard is in good agreement with the value of $99{\cdot}946 \pm 0{\cdot}003\%$ previously obtained.[1] In all cases the limits shown are at the 95% confidence levels for the average.

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Summary—A procedure is described for very precise determination of uranium in high-purity uranium and uranium compounds. Uranium(VI) is reduced in a concentrated hydrochloric acid solution by metallic aluminium in the presence of cadmium ions to uranium(III). This is oxidized to uranium(IV) by protons on addition of an excess of orthophosphoric acid, and then oxidized to uranium(VI) by adding a weighed quantity of potassium dichromate in small excess. The excess of potassium dichromate is determined by constant-current coulometry. The coefficient of variation does not exceed 0·003%.

Résumé—Une description est faite de la méthode très précise de dosage d'uranium dans l'uranium et les composés d'uranium de très haute pureté. On réduit l'uranium(VI) dans une solution forte à l'acide chlorhydrique par l'aluminium métallique en présence d'ions de cadmium vers l'uranium(III). Après oxidation vers l'uranium(IV) par addition d'un excès de l'acide ortho-phosphorique, on oxidise l'uranium(IV) vers l'uranium(VI) par addition d'un excès pesé du dichromate de potassium. On détermine l'excès du dichromate de potassium par coulométrie à courant constant. Le coefficient de variation n'excède pas 0,003%.

Zusammenfassung—Es wird eine hochprezise Methode der Uranbestimmung in reinem Uran und Uranpräparaten beschrieben. Uran(VI) wird in einer stark salzsauren Lösung mit Aluminiummetall in Gegenwart von Cadmiumionen zu Uran(III) reduziert. Durch Zugabe von orto-Phosphorsäure wird Uran(III) zu Uran(IV) oxydiert. Jetzt wird Uran(IV) durch ein genau abgewogenes Überschuss von Kaliumdichromat zu Uran(VI) oxydiert. Der Überschuss an Kaliumdichromat wird durch Culometrie mit konstantem Strom bestimmt. Variationskoeffizient des Verfahrens 0,003%.

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Contributions to the basic problems of complexometry—XXII
Determination of thorium and scandium in the presence of each other

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THE complexometric determination of thorium and scandium in their mixtures was recently described by us.[1] The method is based on the titration of both metals with EDTA at pH 2·5–4 and a subsequent exchange reaction between the thorium–EDTA complex and triethylenetetraminehexa-acetic acid (TTHA) according to the equation:

$$\text{Th–EDTA} + \text{TTHA} = \text{Th–TTHA} + \text{EDTA}. \quad (1)$$

Scandium does not react. Determination of the liberated EDTA and of the excess of TTHA by titration with a zinc solution occurs smoothly according to the equations:

$$\text{EDTA} + \text{Zn} = \text{Zn–EDTA} \quad (2)$$

$$\text{TTHA} + 2\text{Zn} = \text{Zn}_2\text{–TTHA}. \quad (3)$$

The calculation of the amount of thorium and scandium is very simple and is described in the paper cited.

We have now found an easier way to determine thorium in the presence of scandium. The thorium–TTHA complex does not react with phosphate and therefore thorium is not displaced from this complex by zinc; scandium, however, reacts quantitatively. Such a determination is possible only with TTHA, and not with EDTA: thorium and scandium are displaced from their EDTA complexes by zinc in the presence of phosphate, as happens also with the light lanthanides.[2]

EXPERIMENTAL

Reagents

1,2-Diaminocyclohexanetetra-acetic acid (DCTA), 0·05*M*, prepared by dissolving 17·63 g of it in 150 ml of hot 1*M* sodium hydroxide, cooling, and diluting to 1 l. The solution is standardized with 0·05*M* zinc solution.

TABLE I.—DETERMINATION OF THORIUM AND SCANDIUM

Taken, *mg* Th	Sc	Consumption of 0·05*M* DCTA, *ml*	0·05*M* TTHA added, *ml*	0·05*M* Zn used, *ml*	Found, *mg* Th	Sc
58·0	—	5·40	11·00	11·68	58·0	—
58·0	—	5·40	11·00	11·68	58·0	—
58·0	11·24	10·75	11·00	11·60	58·5	11·2
58·0	11·24	10·75	11·00	11·55	58·8	11·1
58·0	22·48	16·10	16·00	21·55	58·2	22·5
58·0	22·48	16·10	16·00	21·45	58·8	22·3
58·0	45·0	26·80	26·00	41·22	59·0	44·8
58·0	45·0	26·80	26·00	41·28	59·6	44·9
34·8	45·0	24·65	24·00	41·40	35·2	44·9
34·8	45·0	24·65	24·00	41·41	35·1	44·9
11·60	45·0	22·50	22·00	41·60	12·1	44·9
11·60	—	1·00	2·02	2·07	11·5	—
34·98	—	2·99	5·06	4·10	35·1	—
116·6	—	10·01	13·17	6·33	116·1	—
174·9	—	15·05	17·22	4·37	174·5	—
11·60	2·35	2·03	3·03	4·13	11·3	2·38
35·0	2·35	4·03	6·07	6·10	35·0	2·27
11·60	11·76	6·10	8·10	14·05	12·5	11·3
11·60	23·52	11·38	15·19	28·15	12·0	23·6
116·6	2·35	11·05	15·19	10·35	116·2	2·32
116·6	23·52	20·43	25·33	30·52	116·8	23·4

TTHA, 0·05*M*, prepared by mixing 24·72 g of it with 150 ml of hot distilled water, adding 1*M* sodium hydroxide and diluting to 1 l. The solution is standardized with 0·05*M* zinc.

Solutions, 0·05*M*, of thorium and scandium were prepared from the nitrates, and of zinc from the metal.

Disodium hydrogen phosphate solution, 1*M*, was prepared by dissolving 35·82 g of it in distilled water, acidifying it to pH 4–5 with 1*M* nitric acid, and diluting to 1 l. Other reagents included a 0·2% aqueous solution of Xylenol Orange and a 20% solution of urotropine.

Procedure

Determination of the sum of thorium and scandium. Titrate an aliquot of the solution at pH 2·5–4 and a temperature of 50° with 0·05*M* DCTA, using Xylenol Orange as the indicator.[1]

Determination of scandium. To a second aliquot add an excess of 0·05*M* TTHA, enough urotropine solution to adjust the pH to 5–5·5, 10–20 ml of 1*M* phosphate, and a few drops of Xylenol Orange. Titrate the solution slowly at room temperature with 0·05*M* zinc solution till the colour changes from yellow to intense red violet. The TTHA consumed corresponds to the amount of thorium. The amount of scandium is calculated by difference from the results of both titrations. Some results are summarized in Table I.

Remarks. The use of two aliquots is necessary. It is not possible, for example, to determine the sum of thorium and scandium by back-titration of the excess of TTHA with zinc, because the colour change is sluggish. (Scandium is slightly displaced from its TTHA complex and immediately hydrolysed.)

Before the end-point, titration with zinc must be carried out slowly, because the last traces of scandium are also displaced slowly from its TTHA complex. The final red violet colour is stable, but fades slightly after 5 min. During the titration a precipitate of scandium phosphate appears, but does not affect the sharpness of the end-point.

DISCUSSION

This method forms part of our systematic study of the common type-reactions:

$$Me_1Y + X + Me_2 = Me_2Y + Me_1X$$

where Y is the anion of EDTA, DCTA, diethylenetriaminepenta-acetic acid (DTPA), 2,3-diaminopropanetetra-acetic acid (MEDTA) or β-hydroxyethylethylenediamine-triacetic acid (HEDTA), where Me_1 = Th, Sc, Y, rare earths, Al, Ti, Cr, Fe, Ga, In, *etc.*, X = a complex-forming, precipitating or extracting reagent such as PO_4^{3-}, $P_2O_7^{4-}$ or F^-, and Me_2 is an ion such as Zn, Pb, Cu or Mn that is used as the titrant.

We have found that these displacement reactions can lead to new and unexpected possibilities in the analytical chemistry of the rare earths (such as their individual determination) or of other combinations of elements which are difficult to analyse in a simple way.

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Summary—A new method for the determination of thorium and scandium in the presence of each other is presented. Two aliquots of the solution are necessary. In one the sum of thorium and scandium is determined by direct titration with DCTA. In the second, thorium and scandium are treated with an excess of TTHA, phosphate is added, and zinc is used to titrate the excess of TTHA and to displace the scandium from its TTHA complex.

Résumé—On présente une nouvelle méthode de dosage du thorium et du scandium en présence l'un de l'autre. Deux parties aliquotes de la solution sont nécessaires. Dans l'une, on détermine la somme du thorium et du scandium par dosage direct au moyen de DCTA. Dans la seconde, on traite le thorium et le scandium par un excès de TTHA, ajoute du phosphate et utilise le zinc pour titrer l'excès de TTHA et déplacer le scandium de son complexe avec le TTHA.

Zusammenfassung—Zur Bestimmung von Thorium und Scandium nebeneinander wird eine neue Methode angegeben. Zwei Teile der Lösung sind notwendig. Im einen wird die Summe von Thorium und Scandium durch direkte Titration mit DCTA bestimmt. Im zweiten werden Thorium und Scandium mit einem Überschuß TTHA versetzt, Phosphat zugegeben und mittels Zink der Überschuß an TTHA titriert und Scandium aus seinem TTHA-Komplex verdrängt.

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TALANTA REVIEW

PROCESS GAS CHROMATOGRAPHY

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Summary—The history of process gas chromatography is described briefly, followed by a description of the essential details of process gas chromatograph systems. The economics of process analysers are contrasted with those of laboratory instruments, and the application of process analysers to automatic control systems, process control computers and data loggers or chemical plant is discussed. The paper concludes with a discussion of likely future trends in the subject.

INTRODUCTION

GAS chromatography, since its discovery some 14 years ago[1] has become a widely used analytical method for the analysis of chemicals and petroleum products. During this time there has been parallel development of fully automatically operated chromatographs in the oil and chemical industries and later by instrument companies. The purpose of these instruments is to analyse process streams continuously to obtain analysis data for process control purposes. In many cases the process operator uses the recorded analysis data to reset process conditions to achieve a desired end. In a smaller but growing number of cases, chromatographs are part of conventional automatic process control systems. Also, process chromatographs are now increasingly being used in feeding analytical data automatically to digital computers which are being used to control and optimize the operation of chemical plants. Process chromatographs are now being used extensively in process research work at the pilot plant stage. Often the data are fed automatically to data loggers.

Since the purpose of the process chromatograph is process control, the emphasis is on relatively high speeds of analysis (repetitive analyses every 10 min and less are now typical). This must be achieved with high reliability for long periods of automatic and largely unattended operation. It must be emphasized that satisfactory results have been achieved only by considerable technical effort by the user. If he does not provide this he may well be disappointed by the results he gets. If he does provide it, chromatographs do give high reliability and good results.

The objectives of this paper are threefold. First, it is intended to describe the significant features of process gas chromatograph equipment. Secondly, it is intended to comment critically on the performance of many commercially available process chromatographs. Thirdly, it is intended to describe the capabilities and use of process chromatographs.

It is worth while pointing out first that process chromatographs are expensive in comparison to laboratory instruments. The cost of a laboratory instrument is typically £600–800 (excluding recorder). The cost of a fully automatic process chromatograph can be as low as about £1,000 for an instrument suitable for simple

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analysis problems. This is not typical in the chemical industry, where instruments of suitable capability cost £2,500–4,000. It is significant that such prices do not usually affect the decision to install an instrument for control purposes. Where on-line analysis is required the annual return is, in many cases, higher than the initial capital cost. The economics behind on-line analyser installation are discussed in detail later in this paper. The disparity in prices between laboratory and process chromatographs has tempted many to buy a laboratory instrument and adapt it to process use. Generally the cost involved has risen rapidly to the point where there has been little difference between the final cost and that of a commercial process chromatograph. The capability and performance of the adapted laboratory instrument may often prove inferior, but in any event manpower is wasted in duplicating work that has already been done in developing the equipment.

HISTORY OF DEVELOPMENT OF PROCESS GAS CHROMATOGRAPHY

The first process chromatographs were built by their users in the chemical and petroleum industries. The first process chromatograph built by I.C.I. was installed at Billingham during 1955, for the analysis of a stream of mixed C_3 and C_4 hydrocarbon gases. Essentially the instrument consisted of a laboratory oven containing the column, thermal conductivity detector and sample injector valve. Apart from the sample injector valve it was very similar to laboratory chromatographs used at that time. The sample injector valve[2] was developed to inject reproducible volumes of gases and liquids into the chromatographic column with an error of less than $\pm 0{\cdot}1\%$. The valve was of the linear sliding plate type. It was pneumatically operated, the air signal being applied *via* a multiway solenoid valve operated from a repetitive process timer. The valve was continuously purged with a steady flow of the process gas, supplied to it from the plant. The component peaks were displayed on a potentiometric strip-chart recorder in the plant control room. The instrument was located in the plant building which was classed as a safe area according to the prevailing fire regulations, but electrical equipment containing sparking contacts was purged with nitrogen as an additional safeguard in the event of sample leakage. During the early days of chromatography similar developments were going on elsewhere with several notable results. These are described below.

The need quickly arose for equipment which would be sufficiently rugged to stand up to plant conditions, which could operate safely in hazardous areas and which could be used in automatic control systems. These developments took place within the chemical and petroleum industries. Subsequently, instrument companies were licensed to produce equipment for sale on the open market. The first of such instruments became available in 1958.

Equipment developed by Phillips Petroleum was produced for wider use by the Perkin–Elmer Corporation. The analyser oven section shown in Fig. 1 consists essentially of a heated and temperature-controlled metal mandrel on to which the columns are wound. The sample valve, column switching valve and detector are attached at one end. At the other end a separately temperature-controlled compartment contains other associated equipment including the carrier gas flow-controller. An insulating cover is fitted over the assembly. An explosion-proof cover is then fitted over the top. This equipment has been very reliable but until recently it has been suitable for straightforward analyses only. Early in the 1960's Perkin–Elmer's

interest in process gas chromatography was taken over by the Mine Safety Appliances Company (M.S.A.). This company have now extended the range of equipment they offer, most of it based on earlier developments by Phillips Petroleum.

Another main development in process gas chromatography was undertaken by the Union Carbide Company. Here the analyser oven consists of a stirred air-bath enclosure. It is essentially an insulated box containing the sample valve, columns, detector, *etc.*, which is purged with a fast flow of hot air. An example of this type of analyser (Beckman Instruments) is shown in Fig. 2. A temperature controller is used to regulate the air temperature by continuously adjusting the power to the air-heater. Analysers of this type are now being produced by Greenbrier-Bendix Instruments and Beckman Instruments in the U.S.A.

A new development by M.S.A. is the production of an analyser using the stirred air-bath enclosure principle with the feature of two separately temperature-controlled compartments. The main compartment is electrically heated and the second compartment is supplied with cold air from a Ranque-Hilsch Vortex Cooler.[3] The maximum temperature difference between the compartments is 75°. This feature makes it possible to operate columns at 0° in the cold zone and other columns at above ambient temperature. This feature greatly extends the range of stationary phases that can be used with a process chromatograph, *i.e.*, to those which are too volatile at elevated temperatures.

In England the process chromatograph came on to the market in 1958 and was made by W. G. Pye & Co. Ltd. of Cambridge. This equipment was developed in conjunction with I.C.I. at Billingham and was based on the Pye Argon Chromatograph. This instrument was equipped with a β-ray/argon detector. The development of this equipment followed a different course from that in the U.S.A., largely because many of I.C.I.'s early process chromatographic analysis problems required the use of a highly sensitive detector. At that time the hydrogen flame-ionization detector had not been discovered, but the β-ray/argon detector[4] was available and had adequate sensitivity. A process chromatograph with β-ray detector was installed on an oxygen plant at Billingham in 1957–58 to measure directly 0–3 ppm concentrations (v/v) of acetylene in oxygen. This chromatograph was home-made and is still giving excellent service. The Pye company is now producing a new range of equipment capable of using the full range of chromatograph detectors, whereas in the past it relied on the β-ray/argon detector.

Since equipment first became commercially available it has steadily improved. Complicated analyses can now be performed in comparatively short times, 10–15 min being typical. Less complicated analyses are commonly performed in less than 5 min. These short times are achieved by using 2, 3 or even 4 columns in conjunction with column switching arrangements. Typical examples will be described. The most frequent concentration range is from 0·1 % upwards, but concentrations of a few ppm are frequently determined with the hydrogen flame-ionization detector.[5,6] At present the analysis data are usually displayed on a potentiometric strip-chart recorder and interpreted by the peak height. Measurement by peak height (instead of peak area) is entirely satisfactory in most cases.

The companies mentioned above have taken most of the initiative in the field of process chromatography. Various manufacturers in Europe produce process chromatographs but these have been later developments and are not significantly different

from previously available equipment. A notable new instrument from the U.S.A. is made by the Foxboro Company. The analyser is not particularly novel in conception (it resembles the Phillips Petroleum type) but it is very well engineered and the presentation of the analysis results is particularly appropriate for process use. Other manufacturers are or until recently have been backward in this respect.

Recently, Elliott Process Automation in the U.K. have brought on to the market a low-cost instrument (Model ISC 1129 at about £1,000 without a recorder) with emphasis on the analysis of single process streams. This instrument was developed originally by the Imperial Smelting Corporation in the U.K. and is suitable for simple analyses where the use of the more sophisticated (and expensive) process chromatographs is unnecessary. This instrument in its present form has been unsuitable for most of the process chromatograph problems in the chemical industry. It has been applicable mainly to problems such as furnace gas analysis and petroleum gas analysis. However, it is now being developed for use on the more complex process streams encountered in the chemical industry. Elliott are also producing under licence another low-cost process chromatograph developed by British Petroleum and called the L.P.G. analyser. This instrument costs about £600 (excluding recorder) and has been designed specifically for measuring a single component in a process stream.

PROCESS CHROMATOGRAPH EQUIPMENT

The component parts of a process chromatograph are shown in the functional diagram, Fig. 3. For descriptive purposes, five main items are described.

1. Analyser unit (constant temperature enclosure and carrier flow control)
2. Programmer unit (including amplifier)
3. Sampling system
4. Services (including carrier gas supply and instrument air supply)
5. Data display

Although process analysers are designed to work out in the open in hazardous areas it is advisable to avoid this. The main reason is that it is much more difficult to maintain the equipment, and maintenance costs go up. The present I.C.I. method of installing process chromatographs is to install items 1–4 of the system in a temperature-controlled, clean-air force-ventilated analyser house located conveniently near to the process streams to be analysed. The analysis data are transmitted to the plant control room and displayed on recorders similar to those displaying the other measured process variables.

Analyser unit

The analyser unit consists of a temperature-controlled enclosure and contains the sample injector, columns and detector. Associated equipment which includes the carrier gas flow-controller and the temperature controller, is part of the unit, but it is contained in a separate compartment, which may or may not be temperature-controlled. The individual components of the analyser are worth consideration. They are (*a*) sample injector valves, (*b*) columns, and (*c*) detectors.

Sample injector valves. Four main types are used; linear slide valves, rotary slide valves, piston valves, and diaphragm valves.

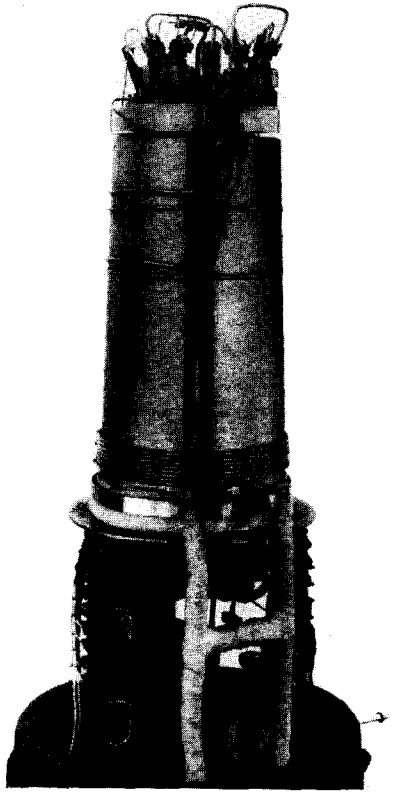


FIG. 1.—Process chromatograph—analyser unit.

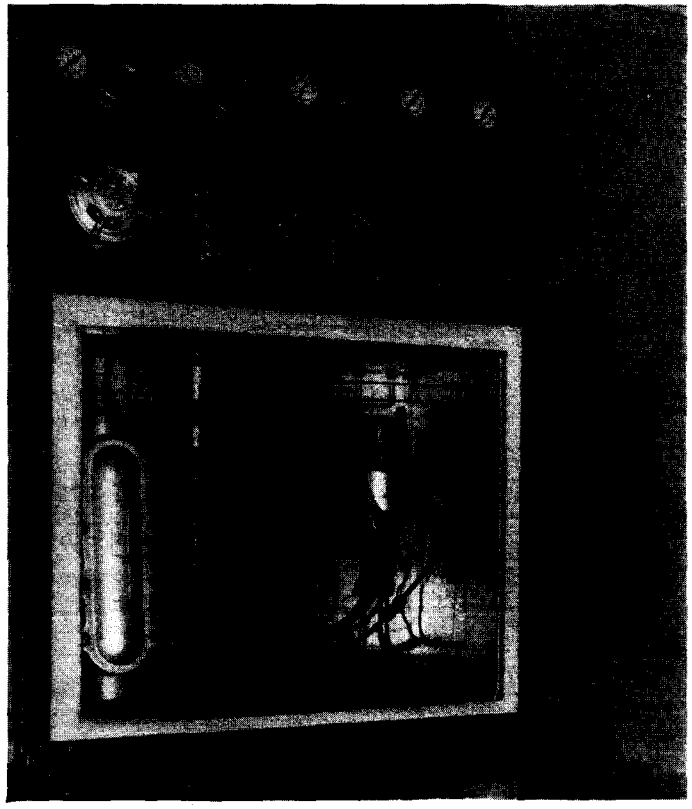


FIG. 2.—Process chromatograph—analyser unit.

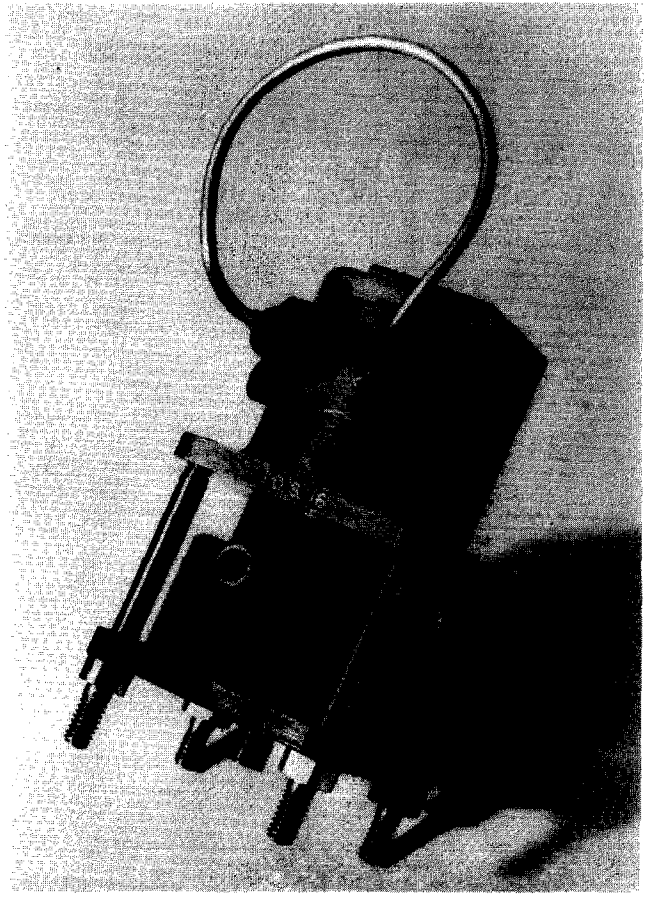


FIG. 4.—Early model of I.C.I. slide valve.

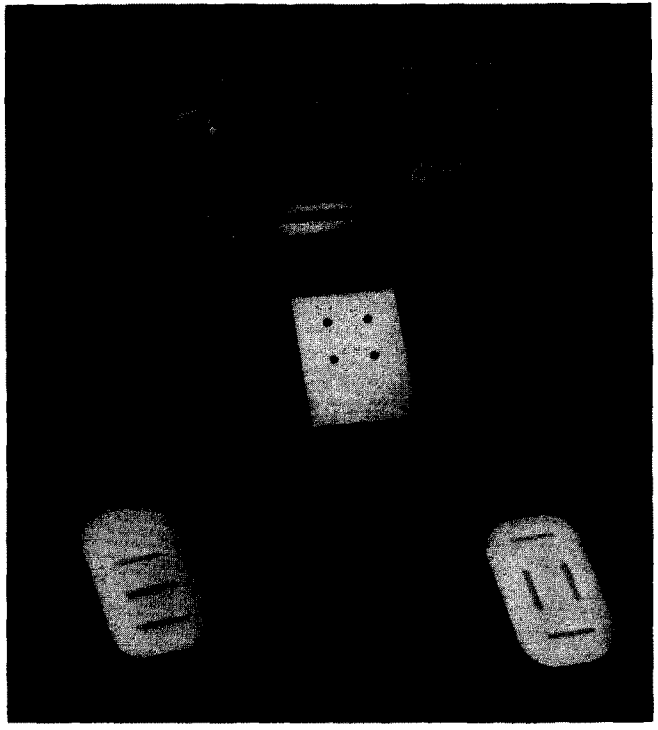


FIG. 5.—Working parts of I.C.I. slide valve.

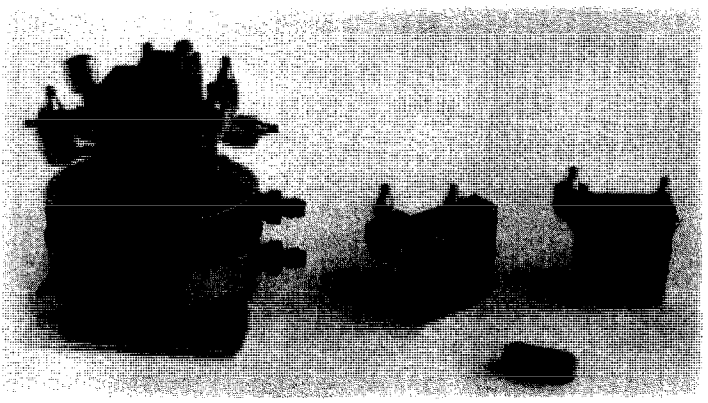


FIG. 7.—Beckman linear slide valve.

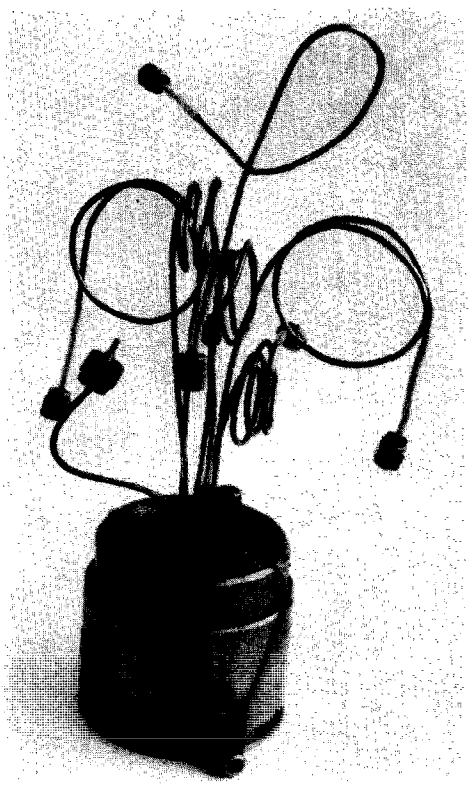


FIG. 9.—Diaphragm valve (Mines Safety Appliances).

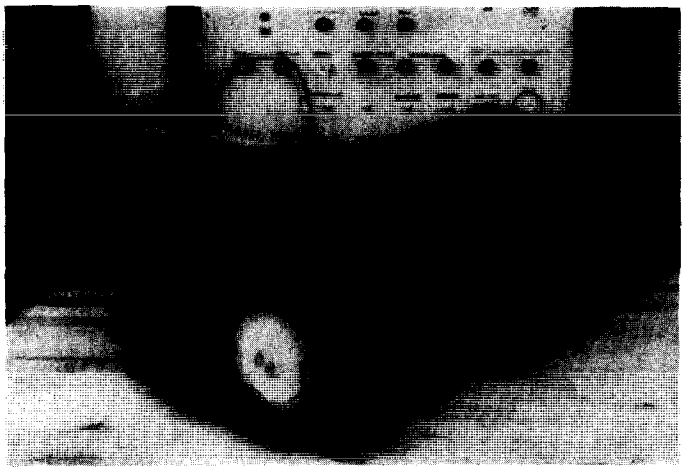


FIG. 14.—Process chromatograph—programmer unit.

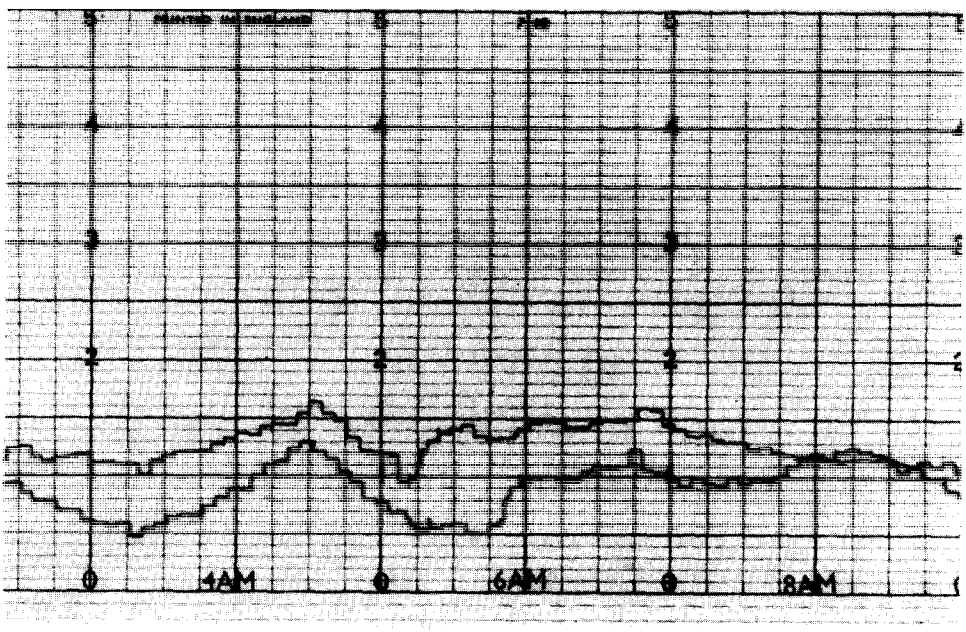


FIG. 16.—Trend output.

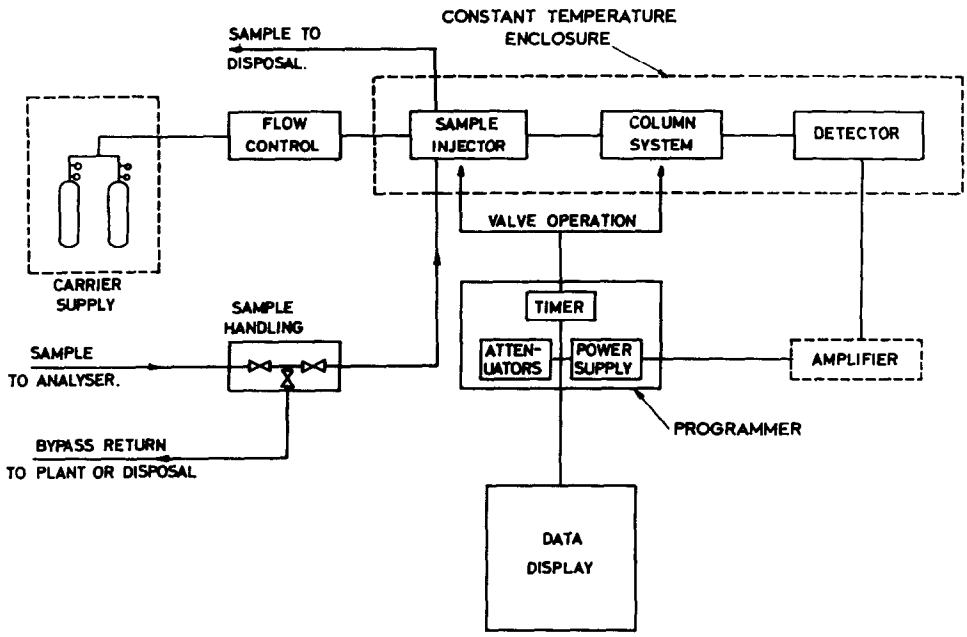


FIG. 3.—Functional diagram of a process chromatograph.

Linear slide valves. Figure 4 shows an external view of a linear slide valve. The working parts are shown in Fig. 5. A 'Fluon'* plastic insert (two examples are shown in Fig. 5) is arranged to slide linearly on the face of the metal block also shown in Fig. 5. Fluon is used because it has a very low coefficient of friction, so a surface lubricant is not required. The surfaces are flat and smooth and are loaded together by a mechanism which ensures sealing. The grooves in the Fluon insert connect various ports in the metal block. Sample injection is achieved as shown in Fig. 6(A) and 6(B). With the insert in one position the sample loop is purged with sample, and with it in the other position the carrier gas flushes the sample into the column. This valve is used in this way to inject vapour samples larger than 0·3 ml. For small volumes, a Fluon insert with grooves as in Fig. 6(C) is used. Here the sample volume is that of the centre groove in the insert. The smallest volume obtainable with this valve is about 1 μl. The sample injection action is shown in Fig. 6(C) and 6(D). This arrangement is used mainly for injecting liquid samples directly into the carrier gas stream.

Figure 7 shows another type of linear slide valve. Here a plastic insert is sandwiched between two metal blocks. The action for vapour sampling is shown in Fig. 8(a) and (b).

The linear slide valve[2] is probably the valve most widely used since its inception in 1954. Its main advantages are that it is not expensive to produce, it is very reliable and it can work at high sample pressures. A sandwich type valve can work reliably with sample pressures up to 500 psig if necessary. For example, such a valve has been used for 9 months at a sample pressure of 200 psig without deterioration. These

* Fluon is the trade mark for ICI Polytetrafluoroethylene. This material is commonly known in the U.S.A. as Teflon (a Du Pont trade mark).

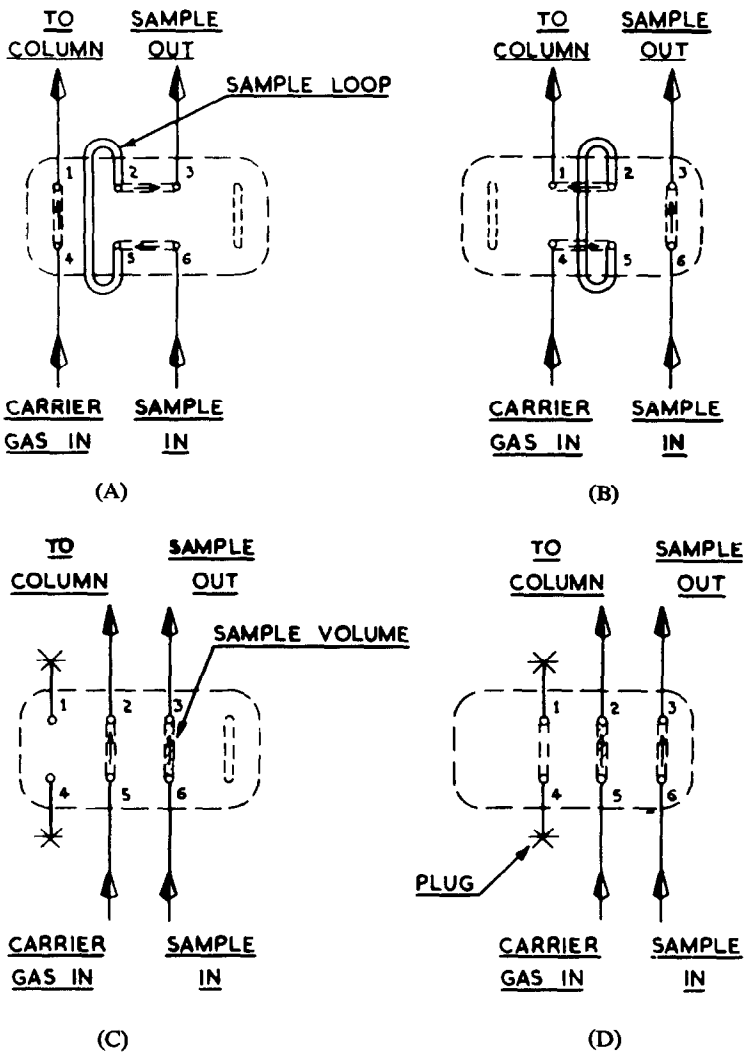
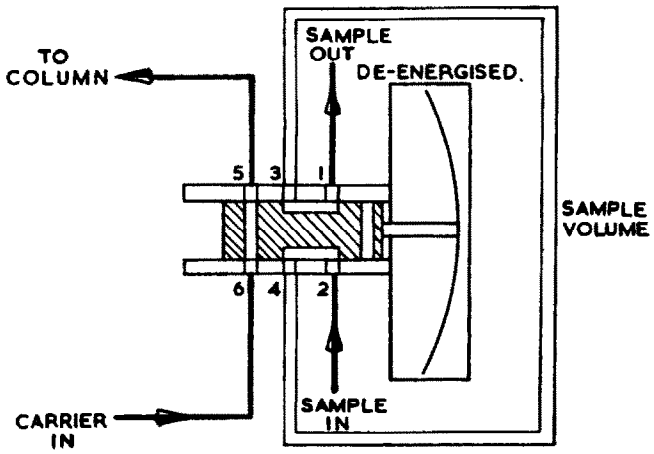


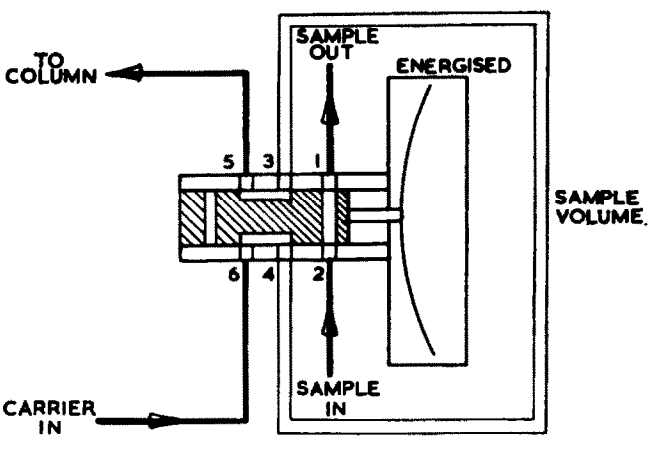
FIG. 6.—Sampling valves with external and internal sample loops.

valves cost about £35 to produce, although they are generally sold at over £100. They are generally provided with six connections, but some are available with eight, so that they can be used for back-flushing as well as sample injection. These valves are all pneumatically operated. Switching of the air signal is usually achieved with a three- or four-port solenoid valve.

Rotary slide valves. In valves of this type a flat-faced insert (usually plastic), into which grooves are machined, is rotated on a flat metal surface. Ports in the surface lead to the external connections. The two surfaces are spring-loaded together. Apart from the rotary action, the operation is similar to that of a linear slide valve. These valves are less popular as they have not proved suitable for high carrier gas or sample pressures since they are generally more difficult to seal. For straightforward problems they do give good performance. They are usually electrically actuated.



(a)



(b)

FIG. 8.—Sampling action of sandwich-type slide valve.

Piston valves. A valve of this type usually consists of a cylinder with connections through the walls at intervals along the axis, together with a piston with rubber sealing rings located in grooves along it. By choice of the appropriate connections, movement of the piston between two positions effects sample injection. These valves are satisfactory for low pressure operation only, as unfortunately the rings tend to flatten and cause leakage. These valves are usually pneumatically actuated. For straightforward problems they give good performance.

Diaphragm valves. These valves are probably the best alternative to the linear slide valve. Unfortunately they are much more expensive and cost two to three

times as much as the linear slide valve. A typical example is shown in Fig. 9. Their operation is illustrated in Fig. 10. The body of the valve is a flat metal surface with 6 ports to external connections, located at the corners of a hexagon. A plastic diaphragm is fitted over the ports and held so that gas cannot leak outwards or inwards but only between the ports. A set of 6 pneumatically operated pistons is arranged, with one piston between each pair of ports. In one of the operating positions of the valve (mode 1) 3 pistons press down on the diaphragm and the other 3 pistons are raised, allowing gas to flow between the ports as shown in Fig. 10. In the other position (mode 2) the pistons previously raised are pressed down and those previously pressed down are raised.

The diaphragm valve has the advantage of very low internal volume, together with ultra high speed of operation. Failure eventually occurs owing to fatigue of the plastic diaphragm. The main disadvantages of the valve are its high cost and the extreme care required in its assembly.

Columns. The columns used in process chromatographs are packed columns very similar to those used in the laboratory, but with the following qualification. Columns are selected for high stability over long periods of operation, preferably 1–2 years but a minimum of 6 months. This precludes the use of the more volatile stationary phases often used in the laboratory, and these stability requirements have also so far prevented the use of capillary columns. These have been found to be unstable, even when the capillaries are coated with the stationary phases which are acceptable for packed columns.

Most process chromatographs use more than one column to perform the desired analysis. This is because a single column is rarely able to perform the analysis satisfactorily in an acceptable time.

Detectors. Three types are generally used: thermal conductivity (katharometer), hydrogen flame-ionization, and β-ray/argon. Other detectors are not in general use mainly because they possess disadvantages for quantitative work. A recent development by Greenbrier Instruments is to use the phosphorus pentoxide electrolytic hygrometer cell[7] in a chromatograph for the determination of water in complex process streams. Most organic compounds poison such cells if used directly. With a chromatograph the water can be separated from other components and then passed alone to the detector. The other peaks are by-passed by a suitable column switching arrangement.

Thermal conductivity. This detector is the one most widely used in process chromatographs. With it, the full-scale range of the process chromatograph corresponds to a concentration range which can be as low as 0–1000 ppm but is more often 0–5000 ppm. Four-element hot wire detectors are generally preferred. The cells used are moderate in size and are generally similar to thermal conductivity cells used in the laboratory.

Hydrogen flame-ionization.[5–8] This detector is the main alternative to the thermal conductivity cell. The detector cells have to be ruggedly constructed so that they are safe for use in plant areas, *i.e.*, they must be able to contain internal explosions and must not propagate a flame to external sources of flammable material. For this reason and also because they require an expensive amplifier, the overall cost of the equipment is £500–800 higher than for equipment with a thermal conductivity detector.

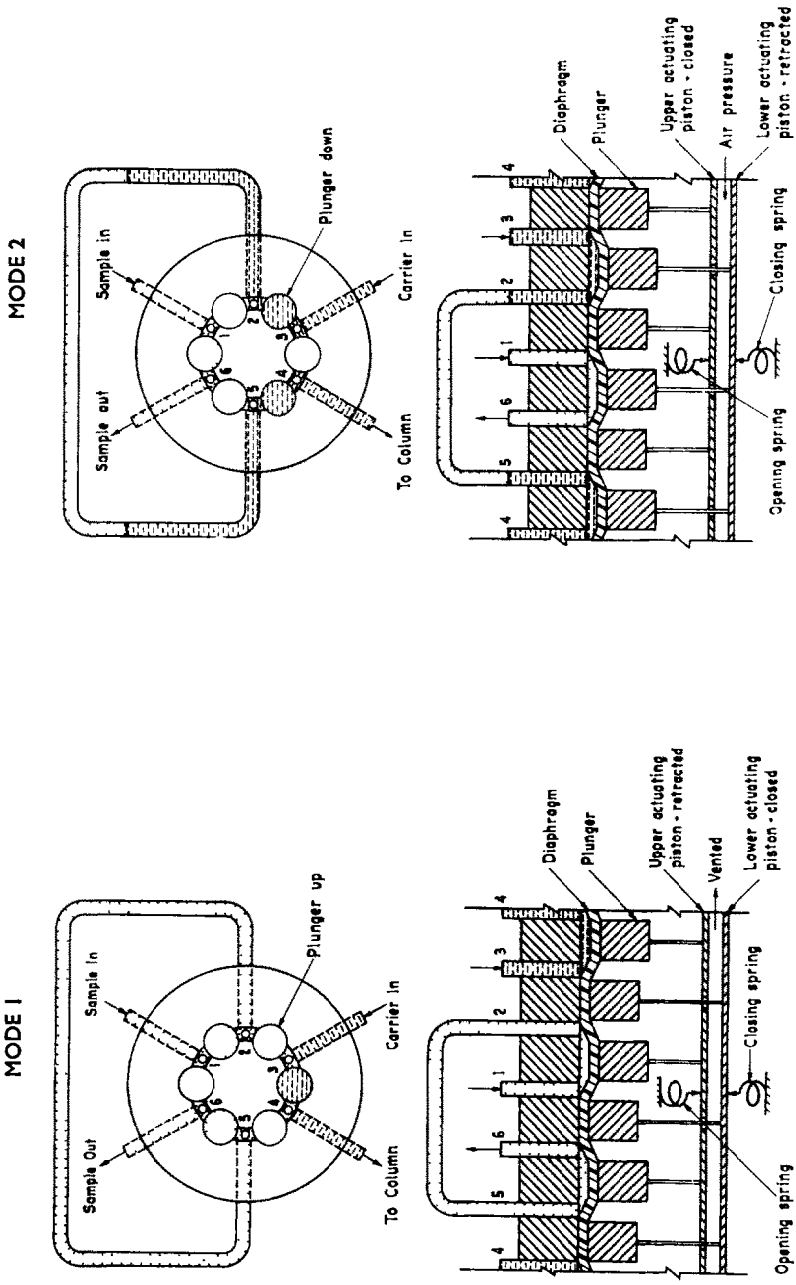


FIG. 10.—Schematic diagram of vapour sampling with a diaphragm valve.

With the hydrogen flame-ionization detector concentrations down to 0–10 ppm can be measured with full-scale deflection. This detector is used normally for those problems which cannot be tackled satisfactorily with a thermal conductivity detector.

β-Ray/argon detector. This detector was widely used in the early days of process chromatography but is much less used nowadays. This is because the hydrogen flame-ionization detecor (a later development) is more attractive for most purposes. It has a wider dynamic range of operation than the β-ray/argon detector and does not have the inconvenience of a powerful radioactive source (^{90}Sr).

Operation of the analyser unit

This is illustrated by two examples.

The first is an analysis performed by an analyser of the type shown in Fig. 1. This analyser has a thermal conductivity detector with a 16-port sample valve mounted

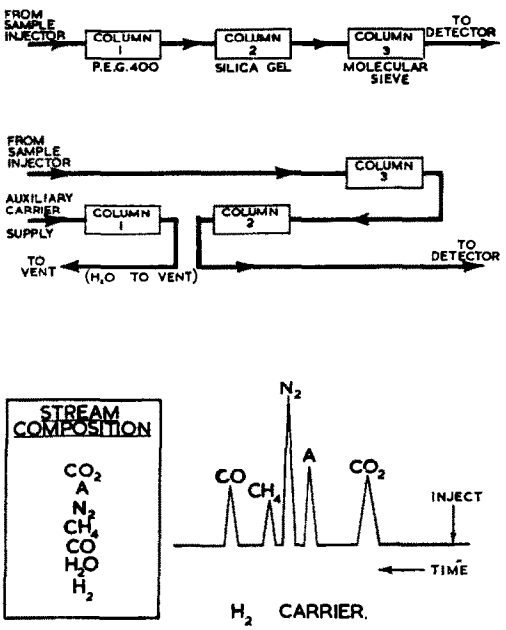


FIG. 11.—Stream analysis with column back-flush through the detector.

on the top of the heated mandrel. The valve actuator is mounted in the lower compartment and is connected to the valve *via* a shaft running through the centre of the mandrel. The flow diagram in Fig. 11 shows how the analysis is performed.

The gas stream to be analysed contains H_2, Ar, N_2, CH_4, CO, CO_2 and H_2O. It is desired to measure all components except the hydrogen and water. To achieve this, three columns are used and are connected to the 16-port valve as in Fig. 12 (CCW) and (CW). The situation before a sample is injected into the columns is shown in Fig. 12 (CW). A steady flow of sample at constant pressure purges the sampling chamber (a length of stainless steel tubing) connected to two of the valve ports. The hydrogen carrier gas is supplied to an adjacent port, and to inject a sample the valve is rotated

to give the flow path shown in Fig. 12 (CCW). Hydrogen carrier gas flushes the sample from the loop into column 1, thence into columns 2 and 3, and finally into the detector measuring cell (SENS). The action of the columns is such that column 1 holds back water but not the other components, column 2 holds back CO_2 but not the remainder. As soon as the remaining components have entered column 3, the valve is shifted to give the flow path in Fig. 12 (CW). The water in column 1 is back-purged out of

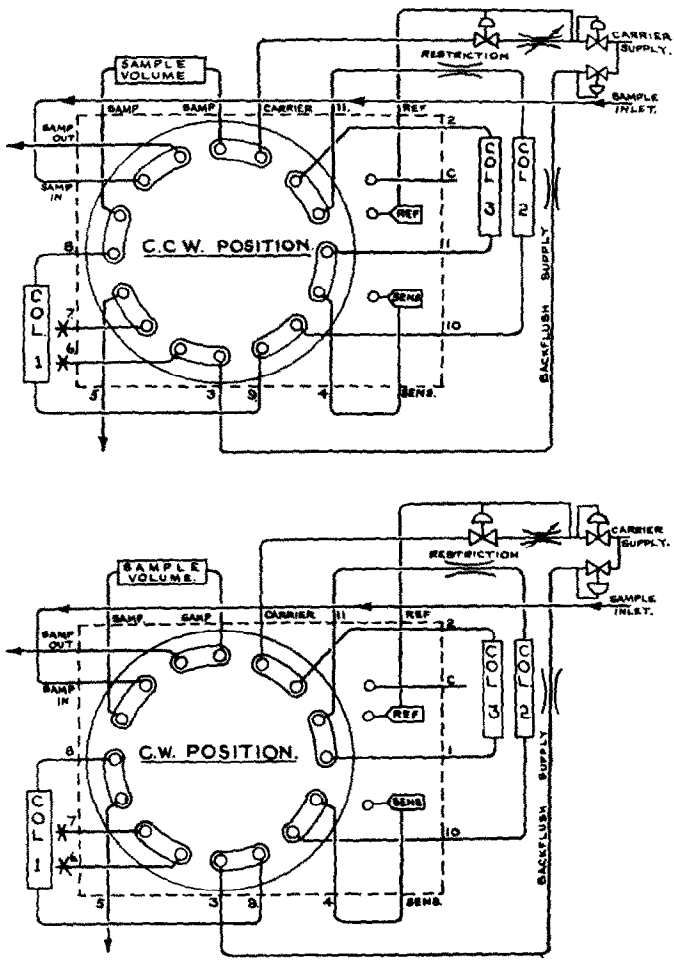
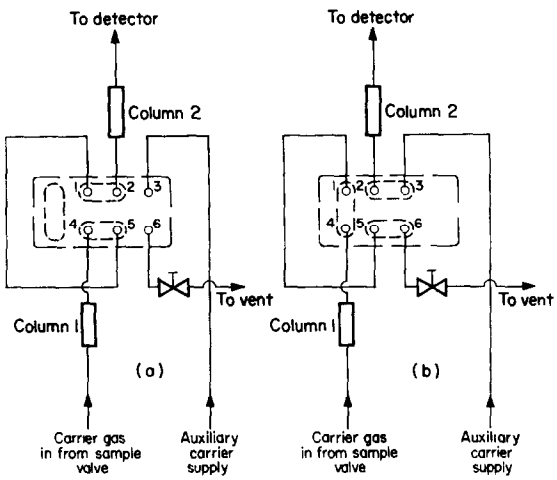


FIG. 12.—Sample injection and column flushing by means of a 16-port rotary valve.

column 1 to atmosphere. The CO_2 peak is back-flushed out of column 2 straight through to the detector where it is measured. The remaining components proceed through column 3 and are separated by it. They pass through column 2 a second time, then to the detector where they are measured. The sort of trace that appears when the detector signal is fully recorded is shown in Fig. 11. The reason for using such a scheme as that in Fig. 11 is that the column material suitable for resolving Ar, N_2, CO and CH_4 (molecular sieves) absorbs CO_2 irreversibly. Thus CO_2 must not be allowed to enter column 3.



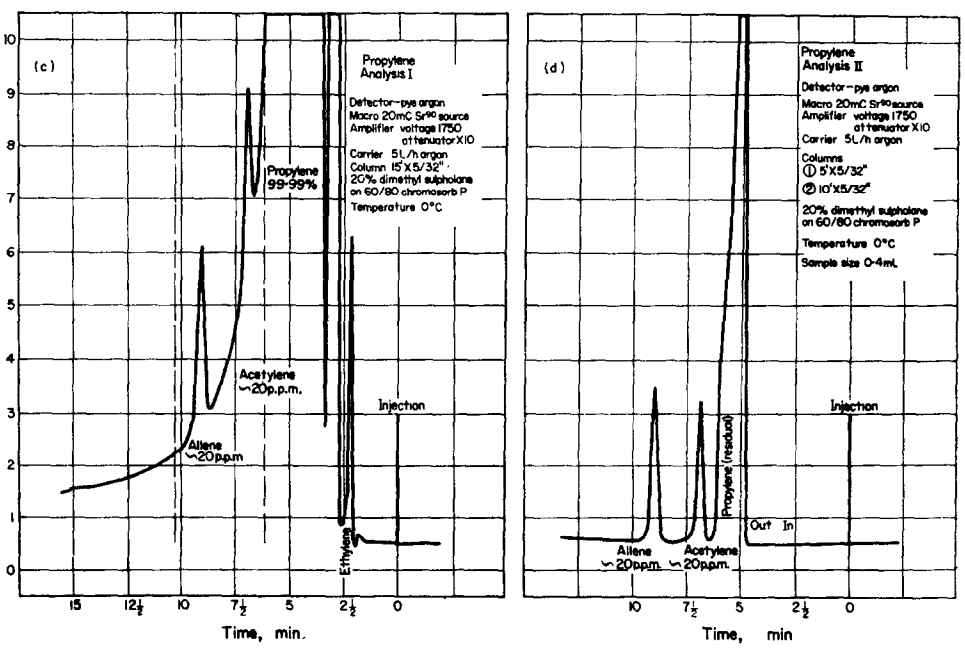


FIG. 13.—Heart-cut analysis.

The second example, of an analysis performed with a β-ray/argon ionization detector, is illustrated in Fig. 13. (This analysis could have been performed equally well with a hydrogen flame-ionization detector.) The analysis problem is the determination of acetylene and allene, each present at about 20 ppm concentration in propylene. Figure 13(c) shows what happens when the sample passes through a single column. The components of interest sit high on the "tail" of the major component. Increasing the column length does not usually help matters. Even if the required

peaks can be separated effectively from the tail, the analysis time is prolonged excessively. Measurement can be made in the laboratory fairly simply. With a process instrument it is necessary to measure the peak height from the zero-base line. This can be achieved by using two columns connected as shown in Figs. 13(a) and (b). Linear sliding plate valves are used, one for sample injection, the other for column switching. The operation is as follows.

With the valves connected as in Fig. 13(b) the sample injector valve is operated and the sample is swept into column 1. The gas emerging from column 1 is vented to atmosphere until the major part of the propylene peak has passed out of the column. The column switching valve is then shifted, Fig. 13(a), to allow that section of the tail of the propylene peak containing the acetylene and allene to pass into column 2. As soon as this section is in column 2, the valve is reversed. Column 2 then separates the two peaks from the peak of the interfering propylene as in Fig. 13(d). The method is known as "heart-cut analysis." A method similar to this was first reported in 1958.[9]

Programmer unit

The programmer by definition controls the operation of a process chromatograph. Since a gas chromatograhic analysis is not a continuous operation but a batchwise process, the essential part of the programmer is an automatic process timer. This timer must initiate at the correct and precisely defined times the series of operations required in the analysis. Also it must repeat this analysis cycle continually. In practice analyses are performed with cycle times ranging typically from 1–40 min. The functions controlled by the timer are; (*a*) sample injection valve operation, (*b*) column switching valve operation, (*c*) automatic zeroing of the detector output, (*d*) processing of the detector output, (*e*) control of the analysis data display and, (*f*) automatic selection of different process streams (where it is desired to analyse in rotation more than one process stream). The programmer usually also contains the power supplies for the detector, and means of signal amplification and attenuation. A typical programmer is shown in Fig. 14.

Process timers. At present these are electromechanical in construction. The commonest type and one which is very reliable consists of an a.c. mains frequency synchronous motor driving a cam shaft *via* gears. The cams (up to 12 in number) are adjustable, and operate microswitches. These switches are used to initiate the various operations, usually *via* hermetically sealed relays. The cycle time of the timer is changed by changing the gearing between motor and shaft. These timers, although reliable, are tedious to set up and adjust. To get over this adjustment problem, other timers use a large diameter disc or endless belt driven at constant speed instead of a small diameter cam. Pins are attached to the disc or belt at positions corresponding to the times an event is to occur. The pins operate a microswitch as they pass it and the switching operation causes a stepping switch (uniselector) to step on one position. The operations are wired through the stepping switch in the correct order. At the end of the sequence of operations in the analysis, the stepping switch is reset by a larger sized pin operating a separate switch. Another variation on this principle is to use a rotating disc with light sources on one side and photocells on the other. Holes punched into the disc are used to permit light to pass through the disc to the photocells at the selected times, and the photocells are used to initiate the desired operations.

Sample and column valve switching. Most process chromatographs now use sample and column switching valves which are pneumatically operated *via* electric solenoid valves actuated electrically from the programmer.

Automatic zeroing. The output signal of a chromatograph detector is subject to random drifts which can become troublesome over periods of several hours. Thus it is standard practice to correct these drifts automatically once per analysis cycle. This is usually done in one of two ways.

1. With the aid of a servo amplifier and a servo motor. The motor is used to drive a potentiometer in the detector signal circuit until the output of the circuit (fed to the amplifier) is restored to zero.

2. A high gain amplifier is connected at the output of the detector, and feeds back its output signal to the detector circuit. The feedback signal is then stored on a capacitor and this corrects any out-of-balance signal from the detector for the rest of the analysis.

Automatic zeroing must always be performed at that part of the analysis cycle when only pure carrier gas is passing through the detector.

Processing of the detector output and control of the data display. The simplest method of recording chromatograph data is as peaks on a strip-chart recorder. Normally the signal is fed to the recorder *via* an attenuator which can be set so that the full scale range on the recorder is equivalent to a convenient figure, *e.g.*, 0–10% concentration by volume. Where more than one peak is measured each peak is allotted its own attenuator. This is necessary as the peak height sensitivity of substances varies greatly. The function of the timer in the programmer is to switch the required attenuators in at the desired times.

More sophisticated instruments store the peak values in memory circuits so that the values can be presented as continuous signals for use for automatic control purposes or fed to loggers or computers for further processing. These more sophisticated forms of data processing are now coming into common use. The function of the programmer is to ensure that the peak signals are correctly stored in the memory circuits.

Automatic selection of process streams. Process chromatographs are often used for multiple stream analysis, *i.e.*, a succession of process streams is analysed in turn by the same instrument. This is usually only possible where the streams are similar in character, *e.g.*, the feeds and products from a group of reactors all producing the same product. The programmer is fitted with a stream selector unit. This may be part of the programmer itself or it may be a separate box. The function of the stream selector is to connect in turn the process streams (usually by energizing electric solenoid valves) to the instrument sample line. The selector is usually a stepping switch, which is stepped on by the process timer in the programmer. The solenoids are wired through the switch.

Sampling system

Any process analyser working continuously on the analysis of a process stream has to be supplied with a fresh and usually steady flow of sample. In all cases a properly engineered sample handling system has to be designed and erected on the plant to provide the analyser with a sample automatically. Owing to the wide range

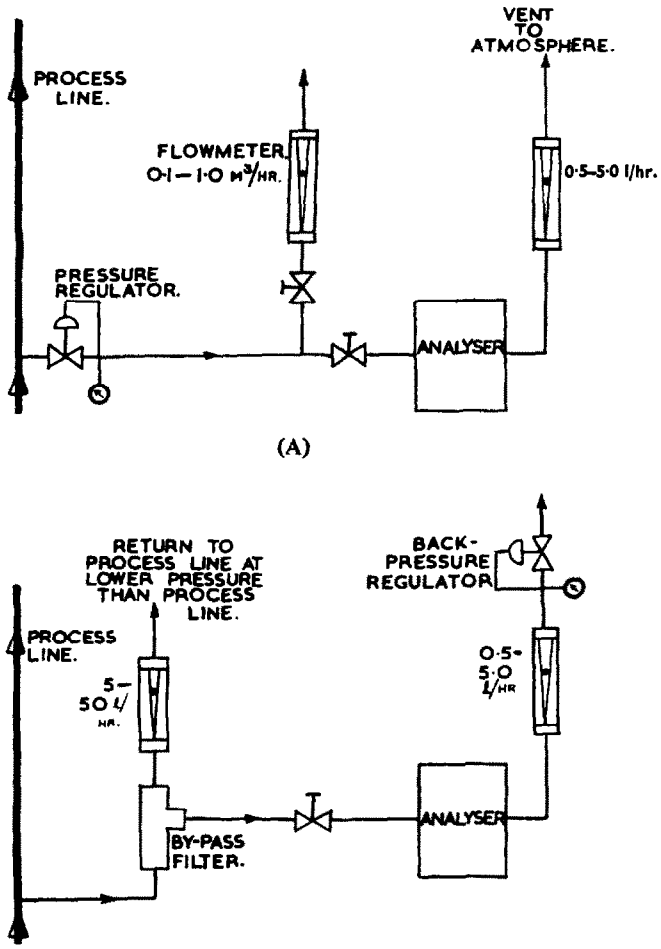


FIG. 15.—Simple sampling arrangements.

of conditions existing in chemical and petroleum processes, sampling system requirements differ considerably.

The individual problems of sampling systems for process analysers are sufficient to justify a separate review. The importance of the subject cannot be overemphasized, and the following points should be borne in mind.

Supplying a continuous sample to an analyser is generally not a difficult task when the sample is a clean liquid or gas under pressure. Figure 15(A) shows a typical system for liquid sampling and Fig. (15)B one for a gas system. Since the analyser may be located up to 200 ft away from the process line, by-passes are used to reduce the lag time from process line to analyser to less than 1 min. Unless the line length is very long, a line of $\frac{1}{4}$ in. outside diameter and $\frac{5}{32}$ in. bore is usually satisfactory.

Difficult problems frequently arise, and in such circumstances a small plant (processing unit) may have to be built to obtain a satisfactory sample. Two examples illustrate this.

(*a*) The process stream is a hot condensible vapour at sub-atmospheric pressure. It contains catalyst dust and inert gases. The analyser requires a cool clean liquid sample under pressure. A processing unit has to be built which removes catalyst dust, condenses the vapour to liquid and removes the inert gases. The liquid is pumped to the analyser. The sample lag-time must be kept below 1 min.

(*b*) The process stream is a hot vapour containing hydrogen, light hydrocarbon gases, gasoline, heavy fuel oil vapour, coke, tars and water vapour. The analyser has to measure the relative proportions of the light hydrocarbons. A processing unit has to be built to remove most of the gasoline and water, and all of the fuel oil, coke and tars, and to supply a clean gas sample to the analyser. If the "heavy" materials are not removed, they would choke the analyser sample lines in a few minutes. The gasoline and water must be condensed out so that the sample entering the analyser is not a mixture of gas and liquid.

In process analysis the objective is rarely to analyse for all the components of the process stream but to determine one or a small number of the components. This can greatly simplify the analyser. In the case of gas chromatography it permits analysis of components present in substances which are themselves not amenable to analysis by gas chromatography *e.g.*, determination of volatile hydrocarbons in solutions containing dissolved polymers and other solids.

Column switching methods are now used extensively to remove unwanted volatile components from a sample being analysed by gas chromatography. Removal of water by such a method was described above. All such methods are really internal sample handling within the analyser.

Sample handling equipment is supplied by manufacturers of process chromatographs. The important thing for the customer is to provide very precise information on his process stream to the instrument manufacturer, if he wishes to obtain satisfactory operation. Many a process chromatograph has earned itself a bad reputation owing to sampling difficulties. Examination of the situation has revealed that the chromatograph itself has worked very well. Unfortunately, an inadequately designed sampling system has not supplied an uninterrupted sample flow to the analyser.

Hard-won experience has convinced the author that detailed design of sampling systems should be done by the user of the analyser and not by the instrument manufacturer. Even where systems are supplied by chemical plant contractors the customer should carefully scrutinize the proposed systems.

Services

Design of the supply of services to process chromatographs is extremely important if reliable operation is required. Two items need particular care, the carrier gas supply and the air supply.

Carrier gas. The supply of carrier gas entering a process chromatograph should be continuous, and pure, dry, and free from organic impurities. Pure gas is usually supplied from cylinders. In the U.K. hydrogen is most commonly used for thermal conductivity detectors and nitrogen for hydrogen flame-ionization detectors. Cylinder gas contains variable amounts of water vapour, often >100 ppm. If this water is not removed, an unstable baseline can result, and damage may occur in the analytical columns, particularly when activated solids are used as column packings. The water

is commonly removed by passing the gas from the cylinder through a drier vessel containing activated molecular sieve pellets.

A molecular sieve drier will also remove many organic materials which might accidentally get into the system. Where flame-ionization detectors are used, all pipework leading from the carrier cylinders to the analyser must be scrupulously clean and free from adsorbed organic substances. Pipework is usually cleaned *in situ*. The first step is solvent washing with methanol and/or benzene. Then the pipe wall is heated along its length with a blow torch and at the same time is purged with a dry inert gas—usually nitrogen from a cylinder. The supply of carrier gas should be uninterrupted. This is achieved by using a pair of cylinders as shown in Fig. 3. Both cylinders are connected to the analyser at the same time, but the pressure-reducing regulators on the cylinders are adjusted so that their output pressures are different by about 5–10 psig. The net effect is for the cylinder with the higher output pressure to deliver gas to the analyser, and the higher pressure prevents the other cylinder regulator from delivering gas. Eventually the pressure in the first cylinder falls to the lower set pressure and the second cylinder then takes over. This prevents failure of the gas supply, say in the middle of the night. An empty cylinder is replaced by the daily maintenance staff on the first morning it is noted to be empty. A further precaution is advisable with carrier gas supplies, in the event of inadvertent failure owing to the onset of leakage (at a pipe joint for instance). It is now normal practice to provide a pressure switch in the carrier line to cut the power supply to the programmer in the event of carrier gas failure. It has the advantages of preventing the burn-out of expensive filaments in thermal conductivity detectors owing to diffusion of air into the detector, and the flooding of columns with sample, which could ruin them.

Air supply. Most, but not all, process chromatographs require a supply of air. The reason for this is historical in that for many years the bulk of chemical and petroleum process instrumentation has been pneumatic. Thus an air supply has been conveniently available and has been used to advantage. The crucial problem which arises here is with hydrogen flame-ionization detectors. These require a flow of air to support combustion, and this air must be hydrocarbon-free. Thus rules out use of air supplies which originate from oil-lubricated compressors. Instrument-grade air used at I.C.I. is oil-free and can be used directly, although a molecular sieve trap is used as an added precaution. The user should examine the nature of his air supply, and if it is not oil-free he must seek another source. Cylinders require frequent replacement, as the normal consumption of a flame detector (20–30 l/hr) will soon empty one. The best solution is a small oil-free air compressor. These are not expensive.

Data display

The satisfactory presentation of the analytical measurements is the most important part of the process chromatograph installation for the process operator. The analysis measurements should be presented similarly to other process measurements such as flow, pressure, level, *etc.*, *e.g.*, as in Fig. 16. The example chosen shows a section of the chart from a standard 2-pen 4-in. pneumatic strip chart recorder. The process stream is analysed for two components. The measured values of each component are stored in the chromatograph programmer. At the same time the stored signal is displayed on the recorder. Each component peak height is changed to the latest value during each subsequent analysis.

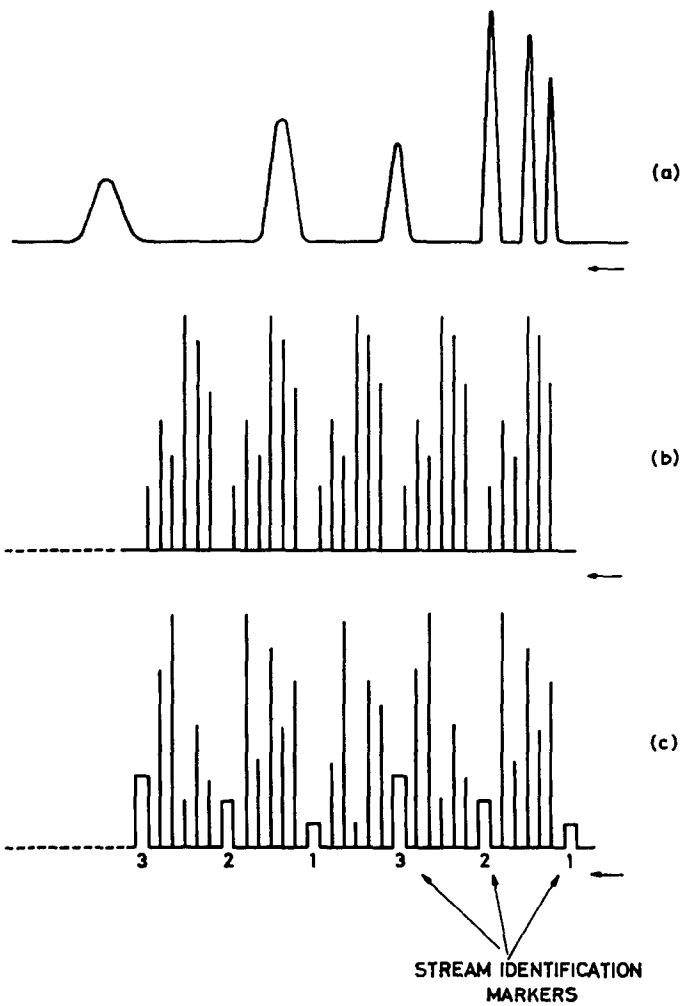


FIG. 17.—Process chromatograph data presentation.

The presentation in Fig. 16 is commonly called "trend" presentation. Each component measured is assigned its own recorder pen. When all the pens are in the same recorder, they have different colours. Thus the process operator can follow the concentration trends easily. The signals are also in a form which is standard in automatic process control systems.

As a process chromatograph is not a continuous analyser but a repetitive batch type of analyser, problems arise in obtaining a display of the kind in Fig. 16. In the laboratory all the user needs is an output on a strip chart recorder as in Fig. 17(a). This is not much use to the process operator who would have to abstract all the peak values from the chart and does not have the time to handle long accumulated lengths of chart. Moreover, with this kind of presentation he cannot easily follow the concentration trends. In the laboratory a chromatograph operator generally measures

the areas of the peaks to obtain the measured values. However, in most cases, measurement with a process chromatograph is made on a peak-height basis. This is possible since under the stable conditions under which process chromatographs operate, the height of a peak is (in most cases) entirely suitable as a direct and accurate ($\pm 1\%$ of full scale) measurement of concentration. Area measurement has been found to be unnecessary in most cases.

Since peak height measurement is satisfactory, the output of Fig. 17(a) is often transformed to that in Fig. 17(b) to avoid excessive usage of recorder chart. This is done by halting the chart drive of the recorder whilst a peak is emerging. With the aid of a time-delay circuit, the chart is advanced a fixed distance between peaks. This form of presentation is called "bar-graph." Its main disadvantage is readily apparent when considered from the process operator's point of view. When the analysis is for more than two peaks, it is very difficult to follow individual component trends. It becomes impossible to do so at a glance when the analyser is used to analyse more than one process stream and all the analysis data are put on one recorder. In such cases the streams are identified by a rectangular marker as in Fig. 17(c).

Bar-graph presentation is suitable if only one or two components are measured in a process stream. Otherwise it is virtually useless. This view is based on the experience of a large number of plant managers and process operators. The only virtue of bar-graph presentation is its low cost. Trend presentation is more expensive, although as a result of recent developments by chromatograph manufacturers, the cost differential has narrowed considerably. It normally does not add more than 10% to the cost of the equipment and in our view this is well justified.

Trend presentation equipment

Various techniques are used for transforming a peak as in Fig. 17(a) to the trend form in Fig. 16. Three basic methods are used: (*a*) phase sensitivity peak pickers, (*b*) diode-capacitor systems, and (*c*) pneumatic peak picking.

Phase sensitive peak pickers. These utilize the electromechanical-servomechanism in conventional potentiometric recorders. For their operation these peak pickers use the property of the change in phase of the a.c. signal which drives the recorder pen motor. The upscale and downscale pen drive signals are opposite in phase. A phase-sensitive circuit is used to detect the change of phase. The output of this circuit is used to permit the pen to drive upscale to the peak maximum but it disconnects the drive motor as soon as the pen starts downscale. The recorder pen is thus held at the peak maximum. The pen is held for a sufficient time (a few seconds) whilst the peak signal is transferred to an auxiliary storage circuit, *e.g.*, a servo-potentiometer, or after conversion into a 3–15 psig air signal it is stored as a pressure in an isolated line.

Our experience with phase sensitive peak pickers is not good; they should be avoided wherever possible. Generally they are difficult to adjust and to keep adjusted satisfactorily.

Diode capacitor systems. In this type of system, the mV output signal from the chromatograph is amplified to give a peak signal of 50 or 100 V maximum value. This is then passed to a diode-capacitor network which allows a capacitor to charge up to the peak value through the diode. The diode back-biases on the tail on the peak, leaving the peak height signal stored on the capacitor. The large signal voltage is necessary to minimize errors due to the nature of a diode's characteristic when only a

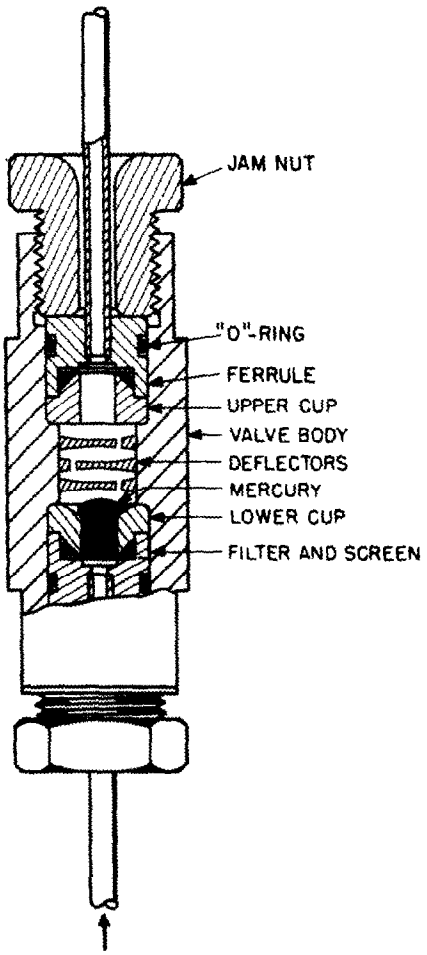


FIG. 18.—Foxboro mercury check valve—construction.

small voltage is applied to it. The peak signal may then be transferred to a second capacitor, leaving the first capacitor ready for the next peak. More sophisticated circuitry based on this principle may be used, usually incorporating integrating amplifier circuits. Generally a diode-capacitor system works very well, and is recommended.

Pneumatic peak picking. A recent development by the Foxboro Company is particularly interesting. Here the electrical signal from the chromatograph is converted into a standard 3–15 psig pneumatic signal by standard process control equipment. The air signal is fed to a novel mercury check-valve consisting of a pool of mercury on a porous metal disc in a cylinder, see Fig. 18. The action is described in Fig. 19. As a peak signal increases from zero the air signal pressure increases from 3 psig. Air bubbles upward through the mercury pool into the chamber above until the pressure has reached that equivalent to the peak maximum. Then the pressure below the pool falls, but, surface tension prevents air from above the mercury pool from seeping back. At this point the peak signal is locked into a pneumatic recorder channel with the aid

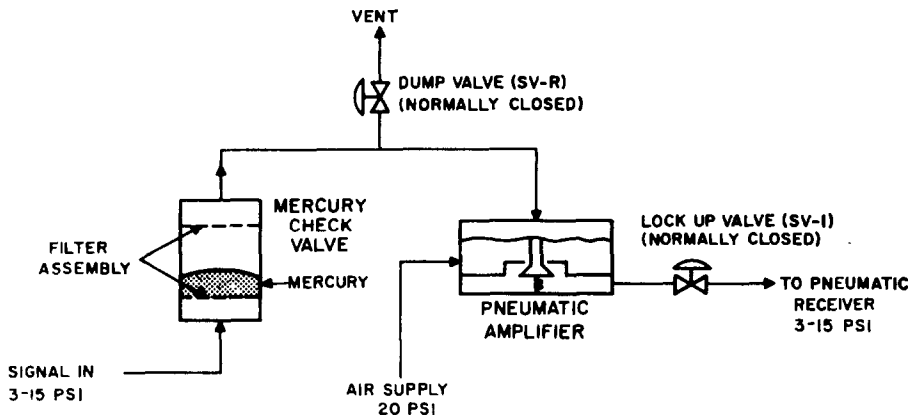


FIG. 19.—Foxboro mercury check valve—operation.

of a leak-free solenoid valve. Owing to the limited air capacity of the system a 1:1 pneumatic amplifier is used as a boost. Another solenoid valve is then used to "dump" the air pressure above the mercury and thus reset the system in time for the next peak. The performance of this system has proved to be very good.

ECONOMICS OF PROCESS ANALYSIS

The intention in installing process analysers (automatic on-line analysers including chromatographs) on running plant, is not necessarily to replace routine shift laboratory analyses and thus economize on personnel, though this may be a bonus. The main reason for installing automatic analysers is that they can do *some* analyses much more economically than shift laboratories can. In many cases it is physically impossible to run and control sections of plant without on-line analysers. This is becoming more so as chemical processes become more and more sophisticated. Furthermore the availability of process analysers makes it possible to design plants more economically, usually by elimination of intermediate storage, and to reduce considerably the periods of production of material that is not of the specified composition or quality.

Process analysers have, of course, to be justified on economic grounds and in these days of sophisticated processes and large scale plant this is easier to do. For instance, chromatographs costing as much as £5,000–6,000 can often be justified.

There are four main reasons for using process analysers in process control.

(*a*) They may be essential for running a plant. In such cases the cost of analysers (several thousands of pounds) is rarely a factor in the decision to build plants (costing several millions).

(*b*) They may be almost essential for running a plant. This situation is best illustrated by a typical example. If the concentration of a key component in a process stream from the bottoms product of a distillation column rises above a critical level it severely upsets subsequent distillation stages in the plant. Such changes in concentration can take place in 20–30 min, making laboratory analysers an ineffective and uneconomic form of control. The quality of the final product can be upset beyond selling specification and the upset in the plant can take at least 24 hr to correct. Thus a day's production is lost, involving loss of profit, and the off-specification product has

to be reprocessed at extra cost. Large-scale plants these days usually produce well over 100 tons of product per day and the value is often in the region of £100 per ton. From this it can be seen that £5,000 for a process analyser is not an excessive price to pay for an instrument. In one recent case it was estimated that a chromatograph costing £4,000 paid for itself in the first weekend it was installed on a plant. This instrument is now regarded as essential.

(*c*) Availability of an on-line analyser may make it possible to design the plant or parts of it more economically. Expensive large storage vessels and tanks may be eliminated and the net capital saving can be large.

(*d*) Improvement in plant running efficiency may be achieved but the case for installing on economic grounds is less easy to prepare. The decision is made only after an exhaustive investigation of the process concerned. The capital cost of the analyser has to be offset by the return based on improved efficiency achieved with the aid of the analyser. A typical situation is the closer control of a distillation column, where economy in operation is achieved by reduced use of steam in the reboiler. The analyser sets the minimum steam flow to achieve the desired composition of the product. This situation arises where conventional control of a column to achieve the desired composition (usually achieved by temperature control) is inadequate.

PROCESS ANALYSERS APPLIED TO AUTOMATIC PROCESS CONTROL

Process analysers are used in automatic control systems for two main reasons. First, they are used if they are essential for controlling stream composition. Secondly, they are used to enable the plant to run at higher efficiency even though they are not required for basic control. Applying process analysers to process control is a highly specialized subject which easily justifies a separate paper. However, a typical situation encountered in practice is illustrated in Fig. 20.

The essential conditions in the bottom part of a distillation column are controlled as shown in Fig. 20(A). Heat in the reboiler is supplied by hot "Thermex"* flowing through it and the flow is controlled by a standard arrangement of a flow-meter, control valve and flow-recorder-controller (FRC). Linked to this is a temperature-recorder-controller (TRC) which monitors temperature several plates up the column. The output of the TRC adjusts the flow setting of the FRC so that a Thermex flow is obtained to give the desired temperature in the column. With the desired column temperature and composition of feed of material to the column, the composition of the bottoms product from the column comes within specified limits. This assumes a number of factors are satisfied, including constant composition of the feed. Unfortunately, if this is not so, merely controlling the column temperature may be inadequate to hold the bottoms product composition to the desired figure. In many cases, however, temperature control is adequate to ensure desired product composition even with feed composition changes.

One example of this type where temperature control is inadequate is now described. It was found that with the situation described above, changes in feed composition, in particular the concentration of one component of a multicomponent mixture, resulted in similar fluctuations in composition of the component in the bottoms product. It

* "Thermex" is an I.C.I. trademark for a high-temperature heat-exchange fluid consisting of a mixture of diphenyl oxide and diphenyl.

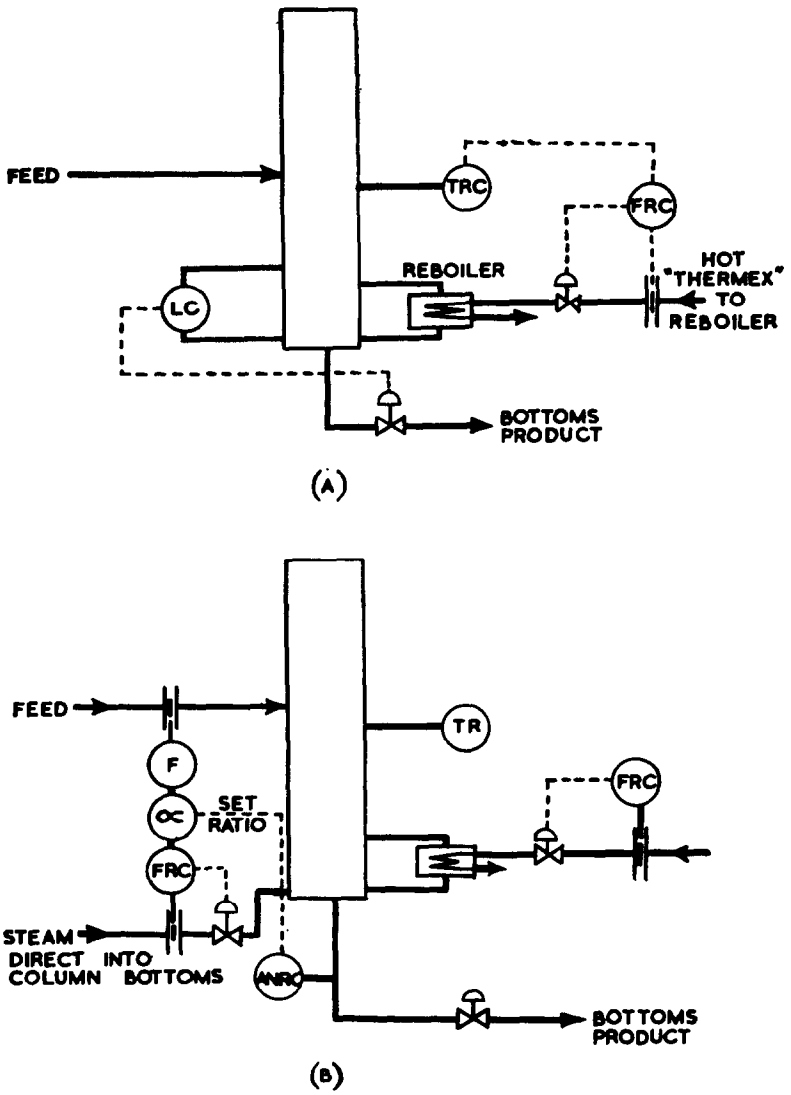


FIG. 20.—Distillation column control.

was very important to hold the level of this component below a certain figure, otherwise severe difficulties were encountered in later stages of the plant. A process chromatograph was installed to monitor the composition of this component on the tray immediately above the bottom of the column. Experiments revealed that the column could be controlled more easily with the system as shown in Fig. 20(B). The flow of Thermex to the reboiler was held constant with the FRC, and the TRC was disconnected from the FRC. Thus the heat flow to the reboiler was held constant. A flow of steam was injected directly into the liquid in the bottom of the column. The effect of this was to lower the boiling point of the liquid and strip off the low boiling unwanted component. The steam flow was controlled with a flow controller FRC and the flow

related directly to the flow of the feed to the column, by a ratio controller (α). Thus if the feed flow rises the steam flow is caused to rise in a pre-set ratio. This system on its own was not adequate to compensate for changes in the composition of the feed, but it was found that if the ratio setting was altered manually in accordance with the observed concentration indicated by the chromatograph, entirely satisfactory control of the composition of the bottoms product could be obtained. The next step was to link the chromatograph output directly into the column control system. This was done by first converting the chromatograph output into the form of a continuous trend signal as described above. The type of signal used was the standard 3–15 psig pneumatic signal used in process control. This was fed to a standard process recorder controller (denoted ANRC) whose output was proportional to the difference between the measured concentration and the desired concentration. This output signal was connected to the ratio controller and used to continuously adjust the ratio between the steam and feed flows. After initial adjustment of the opening conditions and system gain, this system has proved to be entirely satisfactory.

The considerations in applying an analyser in control as in Fig. 20 are principally effectiveness, reliability and operator convenience. The effectiveness of analysers in such situations has been clearly demonstrated. The method of connection is arrived at by thorough system study on the basis of practical results. Reliability is a problem for the instrument engineer and various safety mechanisms are built into equipment to reduce the probability and effects of failure. Operator convenience is achieved mainly by displaying the results in a form compatible with the other process variables he is familar with.

APPLICATION WITH PROCESS DIGITAL COMPUTERS AND DATA LOGGERS

At the same time as process analysers are being used in conjunction with full scale production plants and pilot plants, computers and data loggers are being used to collect data automatically from these analysers. The systems commonly in use at present are illustrated below.

Production Plant → Optimizing computers with conventional automatic control systems
Production Plant → Direct digital control computers

Pilot Plant → On-line data logging equipment → Off-line processing by digital computer

The scope in applying process analysers in automatic control systems is immense. The chromatograph raises special considerations in that the measurement is discrete and made at regular intervals. For control purposes the signal must be as in Fig. 16. The interval between analyses and the delay times in the sampling system must be significantly shorter than the time in which significant changes in the process occur.

If computing or logging equipment is available, the versatility of process analysers can be exploited considerably. The output from analysers can be logged in the "raw" form and printed out in the desired form, *e.g.*, measurements which normally emerge from the analyser expressed as mole% can be printed out as weight %, the computer performing all the calculations. The possibilities are considerable.

The process chromatograph produces its information in a discrete form instead of a

continuous signal. This creates a problem for computing and logging equipment. It is usually tackled in one of the following ways.

Priority interrupt system. As soon as a chromatographic peak emerges the peak value is held by a peak picker (as described earlier). At the same time a separate circuit signals the computer that a peak value is ready to be logged. The computer then stops its previous duty and logs the peak value. The logging operation takes a very short time indeed, usually between 1 and 5 sec. The process is repeated for subsequent peaks. Peaks are identified by the computer either by allocating each peak a separate digital identifying signal which is transmitted from the chromatograph's programmer to the computer, or by letting the computer count up the peaks from the start of the analysis, only a definite known number being selected.

Ordinate sampling. The computer samples the output of the chromatograph detector at regular intervals—say every 1/10 sec. Peak areas and maximum heights are computed by the computer. Start of analysis and peak identification signals are provided separately by the chromatograph programmer. This method is used only where the computer has sufficient spare time.

At present priority interrupt is the most common method. Where trend presentation is available for all peaks of interest, then the priority interrupt method is not required. The peaks can be logged at a time convenient to both the computer and chromatograph.

A recent problem at I.C.I. illustrates the power of a computer. A chromatograph has to analyse 10 similar streams (9 process streams + 1 calibration check stream) in turn and measure 16 components in each stream. The chromatograph measures each component as a mole % concentration. The information required is the amount of each component relative to a key component with the results expressed on a w/w basis. The computer takes all the chromatograph data in, computes the required results, and prints them out as required. At the same time it automatically checks the calibration of the chromatograph by checking its output when analysing a sample of known composition. It corrects the data for calibration errors and checks correct functioning of other parts of the equipment. Additional digital inputs to the computer are provided for this purpose.

INSTALLATION OF A PROCESS CHROMATOGRAPH

The purpose of this section is to emphasize that a process chromatograph is not just an instrument which is placed in a plant area and expected to work, but a complete analytical system. For the system to function correctly it must be correctly designed, installed and maintained. The stages of installation are tabulated below.

(*a*) Initial requirements defined in consultation with the process management.
(*b*) Feasibility of the analyses determined. Information obtained by customer from his own resources and/or the instrument manufacturer. Absolutely all details on process stream(s) composition must be obtained without any omissions of seemingly trivial information.
(*c*) Initial decision to purchase.
(*d*) Specification of analyser, sampling system, services, housing of equipment.
(*e*) Enquiries for the analyser to potential supplier(s) and for the sampling system if to be obtained from the same supplier.
(*f*) Final decision to purchase.

(*g*) Ordering of equipment.
(*h*) Acceptance (after tests and calibration in supplier's factory).
(*i*) Delivery followed by proving trials in laboratory to ensure smooth running of equipment and eliminate unsuspected faults.
(*j*) Installation on site and start-up.
(*k*) Calibration.
(*l*) Maintenance.

Satisfactory results are only obtained if thorough attention is paid to all these stages. The list may seem rather formal and pedantic, but hard-won experience convinces most users of these instruments of the necessity for care at all stages of the installation.

If correct attention is given at the right time a process chromatograph can give excellent results and work reliably. Once the system has reached the maintenance stage the subsequent time and cost required are very low, provided the quality of the maintenance is high.

Typical operating and maintenance costs for a process chromatograph, capital cost £2,500–3,500, (including calibration checking) are estimated as follows.

	£
Personnel costs per analyser per year	150–250
Services and materials (carrier gas, electricity, *etc.*)	100
Total per year	250–350

These costs must be taken only as a typical average. Simple straightforward installations can cost less than the minimum stated. More complex installations can cost considerably more. The user can either employ skilled maintenance personnel—most companies do this—or rely on the manufacturer of the equipment to provide service. At present in the U.K. only one manufacturer provides this service adequately. Perhaps it is significant that this chromatograph manufacturer is the only one who also supplies the full range of conventional process instrumentation.

FUTURE TRENDS IN PROCESS GAS CHROMATOGRAPHY

It appears that gas chromatography is a strongly growing field in the realm of automatic process analysis. It is relevant to consider where changes should take place and what trends are likely.

Reliability

This is the key to acceptance of process chromatographs by plant operating personnel. Regrettably, until recently process chromatographs as received from instrument manufacturers have not been sufficiently reliable. The user has usually been involved in modifications to equipment to make it reliable. Faults have been widespread in type. Typical examples include—unsealed relays whose contacts go open circuit, low quality solenoid valves which overheat and burn out, sample/column switching valves which are prone to sticking owing to use of unsuitable materials.

Fortunately, the reliability of process chromatographs is now recognised by manufacturers as a principal factor in their acceptability to customers.

Speed of analysis

At present, analysis times of 5–15 min are typical and in many cases are adequate. In an increasing number of cases 1–5 min is required where chromatographs are to be connected in automatic control systems. It is envisaged that analysis times of 1–2 min will be regarded as necessary in 5–10 years' time.

Present day instruments are just about adequate for analysers taking 1–5 minutes, but only just so for the shorter times. The limitations of current equipment lie principally in the following parts of the equipment.

Columns. The time factor here is principally determined by the complexity of the sample and by the column size. In the past, columns were generously large and often still are. Smaller-bore packed columns (1/16 in. bore or less) are now becoming more common and are beginning to supersede 1/8 in. bore or larger columns typically used for slower analyses. The disadvantage of using smaller-bore columns is the need to use smaller samples. Where thermal conductivity detectors are used these have to have low internal volume and fast response. Capillary columns have proved disappointing so far owing to their short life. For the immediate future an intermediate between the capillary column and the packed column appears to be the solution for high speed analysis.

Sample and column switching valves. At present the sample and column switching valves have to perform about 50,000 operations per year when performing an analysis every 10 min. The valves described earlier in the paper can achieve this task without failure. Some of these valves do not last much longer than a year, however, without needing overhaul.

For higher speeds of analysis (*e.g.*, one a minute) a valve will have to have a minimum of life of 500,000 operations. This kind of life can be achieved, but careful design is required.

The diaphragm type of valve, if properly assembled, is capable of giving the required life. So is the linear sliding plate type of valve, provided the grade of the Fluon plastic insert material is correctly chosen and considerable attention is paid to the surface finish of the working parts.

In our experience the filled type of PTFE plastics are unsuitable for use as inserts in linear slide valves unless the filler material is graphite. There is a tendency for the filler material to be desorbed from the insert and deposited on the metal faces of the valves, gradually building up and eventually causing valve seizure. In some cases the sample has attacked the filler material and leakage has resulted. Generally speaking pure PTFE polymer is preferred as the insert material. The surface finish must be excellent. A criticism of liquid sampling valves with PTFE inserts is that they give poor reproducibility owing to distortion of the plastic under pressure. This is overcome by using a metal insert sandwiched between metal plates coated with a PTFE layer.

Pneumatic actuation of valves, as used at present, should be adequate even with the higher speeds of operation envisaged in the near future.

Programming and data handling. For higher speeds of analysis coupled with high reliability, it will be necessary to eliminate many electromechanical components from the present equipment. The new equipment will make use extensively of electronic digital techniques in switching and timing of events in the analysis. Signal handling

will have to be all-electronic with the elimination wherever possible of slow servo-balancing potentiometric recorders. Pneumatic peak picking will be too slow, although for control purposes where a pneumatic signal is required for a control valve, the electrical signal will be transduced locally near the valve. Trend presentation of the data will be essential and where process computers are used the chromatograph programming will be performed by the computer.

Temperature programming

This technique is used in the laboratory to advantage in speeding up and improving analyses. It is not used in process chromatography except in rare cases and even then as a last resort. The main problems which arise are "ghosting" and baseline correction as well as the problem of the reliability of the programming device. Ghosting is the appearance of spurious peaks owing to the desorption of stationary phase from the column, caused by repeated cycles of temperature increase and decrease. Baseline drifts are troublesome as most detectors, when connected to columns, are sensitive to temperature and flow changes. Compensation is difficult to achieve satisfactorily.

It is our opinion that the use of temperature programming techniques in process chromatography will not be widespread owing to the above-mentioned difficulties. If it is necessary to analyse samples having a wide boiling range it is probably better to use two chromatographs, one for the "light ends", the other for the "heavy ends." It appears that carrier gas flow programming may prove to be more suitable with process chromatographs.

Detectors

As stated earlier, the detectors used most frequently at present are the thermal conductivity and hydrogen flame-ionization detectors. These are likely to continue as the most widely used detectors. However, there is a tendency towards the use and development of detectors which are highly specific towards certain substances. For instance, the phosphorus pentoxide electrolytic hygrometer cell[7] is used for determination of water in process streams. Other detectors include the piezoelectric quartz detector[8] which is coated so that it can respond to selected materials. Ionization detectors of various types may also be developed to give selective responses.

Zusammenfassung—Die Geschichte der Prozeß-Gaschromatographie wird kurz beschrieben. Dann werden die wesentlichen Bestandteile von Systemen zur Prozeß-Gaschromatographie erläutert. Die Wirtschaftlichkeit von Prozeß-Analysengeräten wird mit der von Laboratoriumsgeräten verglichen, und die Anwendung von Prozeß-Analysengeräten bei automatischen Regelgeräten, Rechenanlager zur Verfahrenskontrolle, Datenspeichern oder im chemischen Betrieb wird diskutiert. Die Arbeit schließt mit einer Erörterung wahrscheinlicher Zukunftsentwicklungen auf diesem Gebiet.

Résumé—L'historie de la chromatographie en phase vapeur industrielle est brièvement décrite, et suivie par une description des détails essentiels des systèmes de chromatographes en phase vapeur industriels. On met en opposition les économies des analyseurs industriels et des instruments de laboratoire, et l'on discute de l'application des analyseurs industriels aux systèmes de contrôle automatique, aux calculateurs de contrôles industriels et aux enregistreurs numériques ou aux installations chimiques. Le mémoire conclut par une discussion sur les tendances futures vraisemblables dans ce domaine.

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PRECIPITATION OF NICKEL SALICYLALDOXIMATE FROM HOMOGENEOUS SOLUTION

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Summary—The reaction between hydroxylamine and salicylaldehyde in the presence of nickel ions has been made the basis of the precipitation of nickel salicylaldoximate from homogeneous solution. Conditions for quantitative precipitation of nickel when present alone or with such metal ions as Fe^{3+}, Cr^{3+}, Al^{3+}, Zn^{2+}, Mn^{2+} and Cd^{2+} are described. The recommended procedure is shown to be useful in the analysis of a steel sample.

THE advantages of precipitation from homogeneous solution (PFHS) over the conventional precipitation techniques have been recognized and demonstrated with great success in recent years. Methods have been suggested for the preparation, *in situ*, of such reagents as dimethylglyoxime,[1] 8-hydroxyquinoline,[2] cupferron,[3] 8-hydroxyquinaldine,[4] and others,[5] thus modifying the well-established gravimetric procedures for the analysis of several metals. The compact crystalline precipitates formed by PFHS are generally purer and easier to handle analytically.

Salicylaldoxime was first reported by Ephraim[6] as a reagent for the detection and determination of copper and nickel. Since then the use of this reagent has been extended to the detection or determination of iron, zinc, bismuth, copper, cadmium, and lead.[7,8] However, only copper has received much attention, and procedures have been worked out for its determination either by direct weighing of the copper salicylaldoximate[9] or by extraction of the chelate into n-amyl acetate and measurement of the absorbance of the solution.[10] An indirect method, reported by Flagg and Furmann,[8] is based on the decomposition of the chelate by excess of iron(III) in hydrochloric acid and titration of the resultant iron(II). Only one study on the determination of nickel with salicylaldoxime has been reported.[9] Vogel[11] has suggested that a few metals such as silver, lead and mercury do not interfere in the determination of nickel, but that there is marked interference by iron, cobalt and copper.

Pietrzak and Gordon[12] have shown that copper salicylaldoximate can be precipitated from homogeneous solution, and that the chelate thus obtained is easy to filter off. Surprisingly, however, the determination of copper by this method was found to be less satisfactory than the conventional procedure.

The present study was undertaken to examine the precipitation of nickel salicylaldoximate by PFHS and to use the procedure for the determination of nickel in a steel sample.

EXPERIMENTAL

Reagents

Metal ion solutions. Solutions of appropriate amounts of metal salts were made in distilled water, filtered and diluted. The nickel solution was standardized by precipitation of nickel dimethylglyoximate by the procedure of Salesin and Gordon.[1]

Salicylaldehdye. About 4·0 g of the reagent were stirred into 1 l. of distilled water. Complete dissolution was ensured by stirring for about 6 hr. The solution was stable for at least 48 hr.

All other chemicals were reagent grade. The pH measurements were made with a Radiometer pH meter, and a filtered ammonia solution (1 + 2) was used for pH adjustments.

Procedure

Place an aliquot of solution, containing 2–75 mg of nickel, in a 400-ml beaker, add ammonium chloride (1–2 g) and an 8-fold excess of a hydroxylamine hydrochloride solution. Adjust the pH to 5·9–6·8 with the ammonia solution. Add a few ml of the salicylaldehyde solution and wait until a turbidity appears. Then add enough salicylaldehyde solution to make the total aldehyde concentration 3–15 times the stoichiometric requirement. Let the solution stand for about 4 hr at room temperature and then filter, using a medium porosity sintered glass crucible, wash the precipitate with distilled water and dry it at 105–110° to constant weight.

Separation of nickel from other metals

The sequence of addition of the reagents is the same as that given above except that tartaric acid (2·0 g) must be added before the pH is adjusted. The amounts of hydroxylamine and salicylaldehyde have to be increased proportionately, taking into account the consumption of the reagent by the cations of metals such as zinc, cadmium, manganese, vanadium, chromium and iron, which form soluble complexes with it. However, in the presence of large amounts of iron (~100 mg), the procedure must be further modified: the reaction time should be at least 14–16 hr; the amount of salicylaldehyde must be in 20- to 25-fold excess of the theoretical amount and can be added all at once; about 3 g of tartaric acid should be added; the hydroxylamine hydrochloride must be in 200-fold excess of the stoichiometric requirement.

Analysis of filtrates for nickel

A few representative filtrates were taken and evaporated almost to dryness. The organic content of the residue was destroyed by repeated addition of nitric acid and evaporation to dryness. The residue was then dissolved in distilled water and the nickel content was determined colorimetrically.[18] In all cases the amount of nickel was found to be $<0{\cdot}04$ mg.

RESULTS

The results obtained by use of these procedures are shown in Figs. 1 and 2, and Tables I–IV. For comparison, a few determinations were carried out by Riley's

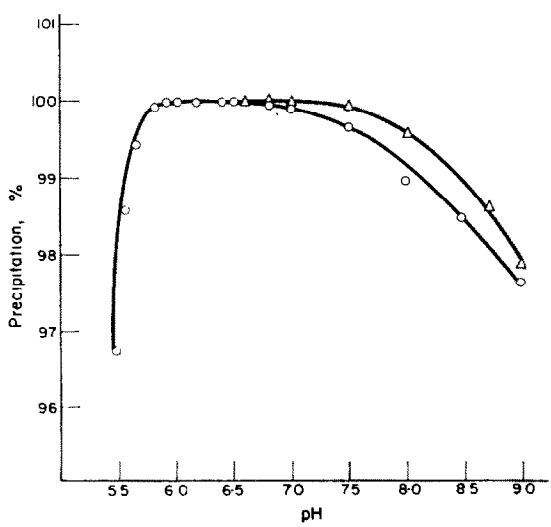

FIG. 1.—Effect of pH on precipitation of nickel salicylaldoximate.
○—standing time 4–6 hr; △—standing time 12 hr.

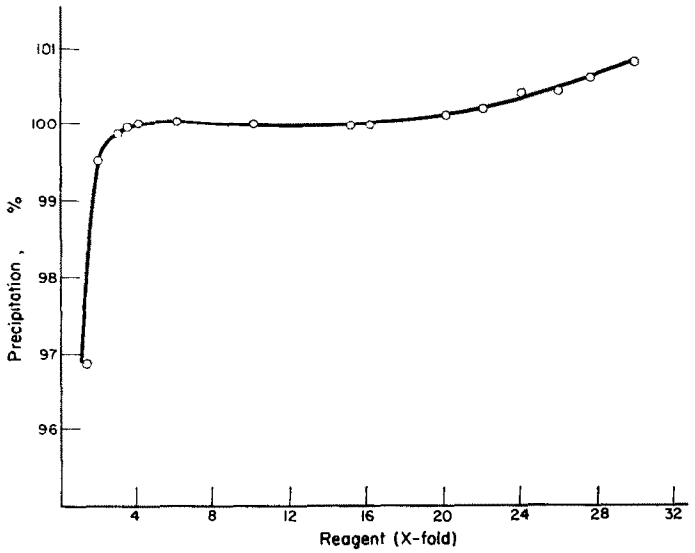

FIG. 2.—Effect of excess of reagent on precipitation of nickel salicylaldoximate.

TABLE I.—COMPARISON OF THE CONVENTIONAL AND PFHS METHODS OF PRECIPITATING NICKEL SALICYLALDOXIMATE

Nickel taken, *mg*	Error in amount found, *mg*	
	Conventional	PFHS
2·12	−0·06	−0·01
	−0·06	−0·02
	−0·07	−0·01
10·62	+0·05	−0·01
	+0·06	±0·00
	+0·08	−0·01
	+0·08	−0·03
21·24	+0·08	−0·01
	+0·08	−0·02
	+0·10	±0·00

TABLE II.—EFFECTS OF SOME DIVERSE IONS ON THE PRECIPITATION OF NICKEL SALICYLALDOXIMATE

	Foreign ion							
	Tartrate (NH_4)	Mn	Zn	Al	Co	Cr	Cu	
Amount taken, *mg*	2000	50	100	100	20	50	50	10
Error in amount of nickel found, *mg*	−0·02	−0·02	−0·01	−0·02	+3·0	+0·01	+5·0	1·0
	−0·01	−0·03	±0·00	+0·01		−0·02		
	+0·01	±0·00	+0·02	−0·01		−0·02		

The amount of nickel taken was 10·62 mg, and 2·0 g of ammonium tartrate were added.

TABLE III.—THE EFFECT OF IRON ON THE PRECIPITATION OF NICKEL SALICYLALDOXIMATE

Excess of reagent added, *x*-fold	Tartaric acid added, *g*	Error in weight of nickel found, *mg*	Iron found in precipitate,* *mg*
15	3·0	−0·12	0·00
20	2·5	+0·01	0·08
		+0·06†	0·05
20	3·0	−0·06	0·01
20	3·5	−0·06	0·00
20	4·0	−0·09	0·00
24	3·0	−0·05	0·06
25	2·5	+0·10	0·10
25	3·5	−0·06	0·02
25	6·0	−0·20	0·00

* Determined colorimetrically by the thiocyanate method.

† A reaction time of 18 hr was allowed. For all other determinations the period was 15 hr.

The amount of nickel taken was 9·92 mg, and about 100 mg of iron(III) were added. A 200- to 300-fold excess of hydroxylamine hydrochloride was used.

TABLE IV.—DETERMINATION OF NICKEL IN A STEEL SAMPLE

Aliquot taken, *ml*	Nickel found, %	Iron in precipitate, *mg*	NBS Certificate value for nickel present, %
25·0	11·06	0·00	11·14
	11·05	0·00	
	11·08	0·02	
50·0	11·06	0·00	
	11·12	0·04	
	11·18	0·06	
	11·19	0·06	
	11·12	0·02	
	10·00*	0·08	
	11·89†	0·65	

* Conventional procedure, time of standing, 6 hr.

† Conventional procedure, time of standing, 16 hr.

method.[9] He suggested that an excess of reagent should be added and the solution stirred to coagulate the precipitate. In the present work a two-fold excess of the reagent was added to the metal solution at pH 6·0–6·5. The solution was stirred and then allowed to stand for 3 hr before filtration. The results are presented in Table I.

The behaviour of iron in this system deserves special mention. Citric acid, EDTA and tartaric acid were tried as masking reagents. Tartaric acid was found to be suitable, but citric acid and EDTA prevented the precipitation of nickel salicylaldoximate. However, with the procedure outlined above, the amounts of tartaric acid and hydroxylamine hydrochloride must be kept within certain limits to give quantitative precipitation of nickel. Amounts of tartaric acid below a minimum value gave positive errors and impure precipitates. Large amounts of tartaric acid gave pure precipitates but low recoveries of nickel. Large excesses of hydroxylamine hydrochloride were required for quantitative recovery. Some of the results of these experiments are collected in Table III.

Analysis of a steel sample for nickel

About 1·0 g of the steel (NBS No. 121b) was dissolved in the usual way and diluted to 500·0 ml. Aliquots (25 or 50 ml) were transferred into 400-ml beakers. Tartaric acid (3·0–3·5 g), hydroxylamine hydrochloride (2·5 or 5·0 g, according to the aliquot) and ammonium chloride (2·0 g) were added to each and the pH was adjusted (6·0–6·5) with dilute ammonia solution. Enough aqueous solution of salicylaldehyde to give a 20- to 25-fold excess was then added. The mixture was set aside for 14–16 hr before filtration. Some results obtained by this procedure are shown in Table IV.

DISCUSSION

This study has shown the expected superiority in the quality of the precipitates obtained by the PFHS method and has established a set of experimental conditions under which the recovery of nickel is quantitative. The procedure suggested, however, failed to achieve a successful separation of nickel from copper. (Copper salicylaldoximate is known to be precipitated in varying amounts from solutions over a wide range of pH.) Cobalt also seriously interferes, but this was not investigated in detail. The precipitation of zinc and cadmium was found to begin at pH 6·5. When nickel was precipitated at pH 6·0–6·3 there was no co-precipitation of these elements. In the presence of tartaric acid zinc did not co-precipitate even at pH 7·0. Hence the use of tartaric acid was recommended. However, when cadmium was present, tartaric acid could not be used because the cadmium tartrate complex is sparingly soluble.

In the procedure of Salesin and Gordon for the determination of nickel, the generating reaction was found to be extremely slow (24 hr standing time required) in the presence of iron. In the present case it was found that large excesses of iron and tartaric acid also retarded the precipitation of nickel. However, it was shown that a proper combination of the amounts of tartaric acid and hydroxylamine hydrochloride did produce a successful separation of nickel from large amounts of iron, within a reasonable reaction time.

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Zusammenfassung—Die Reaktion zwischen Hydroxylamin und Salicylaldehyd in Gegenwart von Nickelionen wurde zur Fällung von Nickelsalicylaldoximat aus homogener Lösung verwendet. Die Arbeitsbedingungen zur quantitativen Fällung von Nickel allein oder neben Metallionen wie Fe^{3+}, Cu^{2+}, Al^{3+}, Zn^{2+}, Mn^{2+} und Cd^{2+} werden beschrieben. Die empfohlene Vorschrift erweist sich bei der Analyse einer Stahlprobe als nützlich.

Résumé—La réaction entre l'hydroxylamine et el salicylaldéhyde en présence d'ions nickel a été prise comme base pour la précipitation du salicylaldoximate de nickel à partir d'une solution homogène. On décrit les conditions de précipitation quantitative du nickel seul ou en présence d'ions tels que Fe^{3+}, Cr^{3+}, Al^{3+}, Zn^{2+}, Mn^{2+} et Cd^{2+}. On montre que la technique recommandée est utile pour l'analyse d'un échantillon d'acier.

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L'APPLICATION DES RADIOISOTOPES A LA CHROMATOGRAPHIE SUR COLONNES DE CELLULOSES SUBSTITUEES—IV*

L'ANALYSE DU MERCURE ET DU ZINC DANS LE BISMUTH

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Résumé—Les radioisotopes ont été appliqués à l'étude du comportement chromatographique de quelques nanogrammes de bismuth sur cellobiose, cellulose et sept celluloses substituées. Toutes les celluloses en éther éthylique adsorbent le bismuth pourvu qu'il soit sous forme de nitrate et qu'un excess d'acide nitrique ne soit pas présent. Le bismuth a été élué à l'aide de thiocyanate en méthanol–éther, ou d'acide chlorhydrique en méthanol, suivant la force de rétention montrée par les différents groupes fonctionnels de la cellulose. Une méthode simple de séparation du mercure d'avec le bismuth en différents rapports est presentée.

CETTE étude a été conduite pour définir le comportement chromatographique du bismuth sur colonnes de celluloses substituées. Les seules indications au sujet de l'adsorption du bismuth sur celluloses sont contenues dans une monographie qui traite la purification de l'uranium d'avec de nombreux métaux parmi lesquels le bismuth qui serait retenu sur cellulose naturelle en éther-acide nitrique.[1]

Comme le comportement de l'arsenic et de l'antimoine a déjà été étudié dans les mêmes conditions,[2,3] les données concernant le bismuth s'ajouteraient à celles disponibles et fourniraient des indications intéressantes sur les possibilités de séparation de l'arsenic et de l'antimoine d'avec le bismuth.

L'étude du bismuth dans les conditions choisies pour l'étude du mercure et du zinc[4] devrait permettre de sélectionner les celluloses qui retiennent particulièrement bien le bismuth, et d'établir les conditions expérimentales favorables à la séparation d'avec le mercure et le zinc.

La détermination du mercure dans le bismuth à haute pureté a été l'objet d'une publication récente[5] qui a été suivie d'une publication sur la détermination du zinc dans le bismuth.[6] La méthode présentée était basée sur plusieurs opérations, parmi lesquelles la distillation finale du mercure et la formation d'un amalgame sur une feuille d'argent. Puisque la méthode radiochimique demandait soit l'introduction d'une quantité de mercure ou de zinc comme entraîneurs, soit l'analyse par spectrométrie gamma, les auteurs cités se sont vus obligés à irradier l'échantillon de bismuth avant même de commencer les manipulations chimiques. Aucune indication n'a été donnée sur la radioactivité de l'échantillon de bismuth après plusieurs jours d'irradiation, mais il faut penser que, comme le ^{209}Bi a une section efficace de 0·015

* Part III—*Talanta*, 1967, **14**, 85.

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barns pour les neutrons du spectre du réacteur,[7] une certaine quantité de bismuth ait subi les réactions suivantes:

$$^{209}\text{Bi (n, } \gamma) \, ^{210}\text{Bi} \xrightarrow[5 \text{ jours}]{\beta^-}$$

$$^{209}\text{Bi (n, } \gamma) \, ^{210}\text{Bi isomère} \xrightarrow[\sim 10^6 \text{ ans}]{\alpha}$$

On doit par conséquent admettre que l'irradiation préalable de l'échantillon à analyser, oblige à manipuler un échantillon radioactif, et que la méthode présente des aspects désavantageux, tels que perte de temps pour laisser décroître une partie de l'activité, télémanipulation, déchets radioactifs.

Au contraire, une méthode basée sur l'activation neutronique des traces de mercure ou de zinc déjà séparées d'avec la matrice de bismuth est plus simple, ne demande pas les précautions demandées par un échantillon radioactif, et évite les interférences qui pourraient provenir de l'activation d'autres impuretés éventuellement présentes dans le bismuth. En d'autres mots, l'activation neutronique doit être la dernière opération à exécuter.

Deux nouvelles celluloses substituées, précisément la sulfoéthyle et la para-aminobenzyle, sont devenues disponibles et ont été prises en considération avec le cellobiose. Ce dernier étant le dimère du glucose, il est intéressant de le comparer avec la cellulose naturelle, car les différences de capacité d'adsorption seraient imputables au fait que le cellobiose est une molécule de petites dimensions, tandis que la cellulose est une macromolécule.

PARTIE EXPERIMENTALE

Solutions

Les produits chimiques et les solvants étaient de degré analytique et ils ont été utilisés sans traitement ultérieur. Les solutions utilisées sont les suivantes.

(*a*) Ether éthylique anhydre.
(*b*) Acide nitrique 90% (2 ml) dissous en éther éthylique (98 ml).
(*c*) Thiocyanate d'ammonium (40 mg) dissous en méthanol (20 ml) plus éther éthylique (80 ml).
(*d*) Thiocyanate d'ammonium (5 g) dissous en méthanol (20 ml) plus éther éthylique (80 ml).
Acide chlorhydrique 0,5, 1,5 et 5*M* dans le méthanol.

Celluloses

Cellulose Whatman CF 11, en poudre, non substituée.
Cellulose Whatman DE 11, en poudre, diéthylaminoéthyle.
Cellulose Whatman AE 11, en poudre, aminoéthyle.
Cellulose Whatman P 11, en poudre, phosphate.
Cellulose Whatman CM 11, en poudre, carboxyméthyle.
Cellulose Whatman ET 11, en poudre, epichlorohydrine triéthanolamine—Ecteola.
Cellobiose Sigma CB, en poudre, (glucose-β-glucoside).
Cellulose Bio-Rad SE, sulfoéthyle.
Cellulose Bio-Rad PAB, en poudre, *p*-aminobenzyle.

Radioisotopes

Le bismuth-207 a été fourni par Science and Engineering Corp, Pittsburgh, Pa, U.S.A. et ses caractéristiques étaient les suivantes: radioactivité 29,0 μC/ml; activité spécifique: carrier-free; pureté radiochimique > 99%. Une fraction de 250 μl de cette solution a été diluée en 10 ml d'acide nitrique 90%. Une fraction de 50 μl de cette dernière solution a été prélevée pour chaque expérience. Les autres radioisotopes correspondaient à ceux qui ont été utilisés dans les autres Parties de cette étude.[2-4]

Mesures de radioactivité

Les fractions d'élution ainsi que les celluloses ont été recueillies en bouteilles de plastique de capacité et dimensions uniformes. Leur radioactivité a été mesurée à l'aide d'un spectromètre gamma à 128 canaux ND-110, couplé électroniquement à un cristal de NaI(Tl), et comparée à un étalon. La dispersion moyenne des résultats des déterminations quantitatives était de 8%.

Préparation des colonnes de celluloses

Les colonnes et le mode opératoire étaient les mêmes que décrits dans la Partie précédente.[4] Les dimensions des colonnes de cellulose étaient 15 cm × 1 cm, et le temps pour compléter deux chromatographies était une heure.

Préparation des solutions à haute concentration de bismuth et de mercure

Du trichlorure anhydre de bismuth a été dissous, et l'hydroxyde a été précipité, filtré et séché. L'hydroxyde de bismuth (0·21 g) a été dissous dans 250 μl de la solution de ^{207}Bi en l'acide nitrique 90%; 100 μl de la solution résultante ont été prélevés pour chaque expérience. La quantité d'hydroxyde de bismuth a été calculée de façon à neutraliser presque tout l'acide nitrique, et à en laisser l'excès nécessaire pour tenir le bismuth en solution dans l'éther. Ces solutions ont été préparées au moment de l'utilisation.

La solution de mercure a été préparée en dissolvant 5 g de chlorure mercurique dans 100 ml d'éther éthylique.

DISCUSSION DES RESULTATS

Les courbes d'élution représentées en Figs. 1, 2, 8, 9 montrent que les celluloses où le bismuth est quantitativement retenu sont la cellulose naturelle CF, la diéthylaminoéthyle DE, la sulfoéthyle SE et la *p*-aminobenzyle PAB, quand la colonne de cellulose est préparée dans l'éther éthylique. Le cellobiose retient aussi quantitativement le bismuth (Fig. 7).

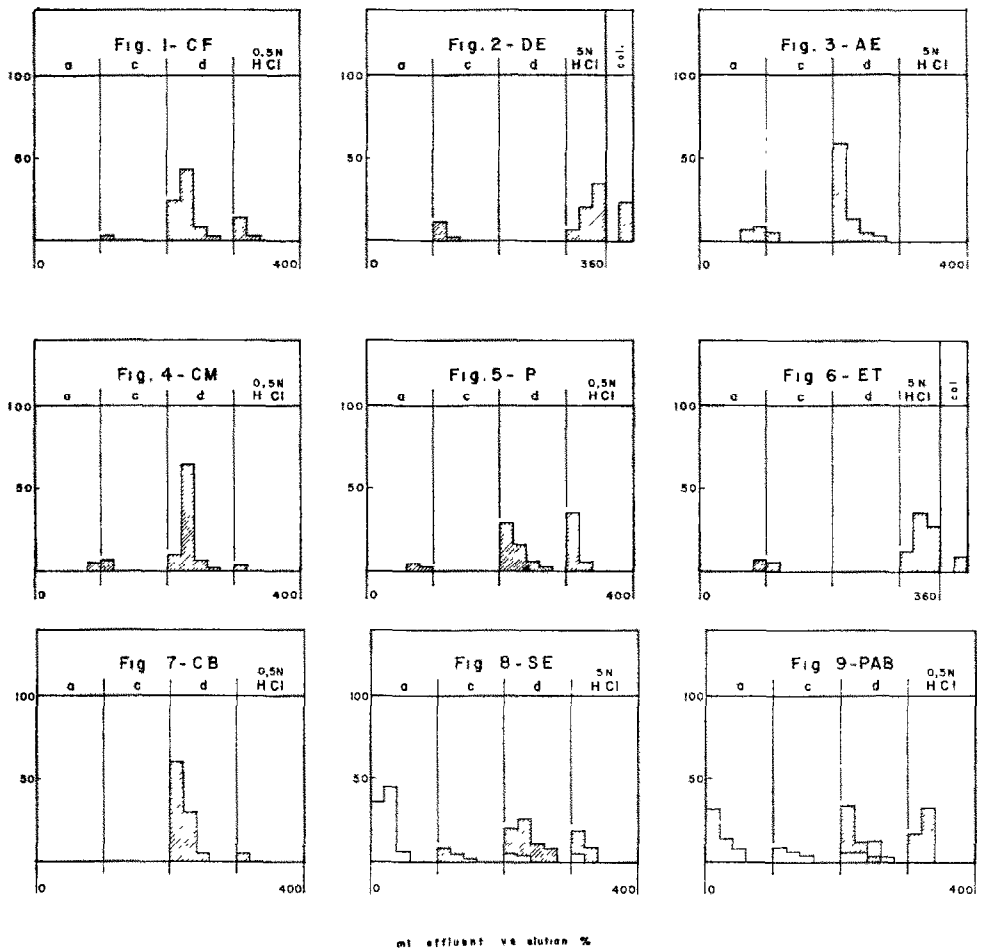
Les autres celluloses AE, CM, P, ET (Figs. 3, 4, 5, 6) laissent passer seulement une petite quantité de bismuth pendant le lavage avec l'éther éthylique, tandis que la quantité la plus importante est fortement adsorbée et peut être éluée avec la solution concentrée (*d*) de thiocyanate ou celle de l'acide chlorhydrique dans le méthanol, sauf pour la cellulose Ecteola ET sur laquelle reste le 10% du bismuth.

La cellulose Ecteola ainsi que la diéthylaminoéthyle adsorbent particulièrement bien le bismuth à tel point que l'acide chlorhydrique 5*M* n'a pas la capacité d'éluer le bismuth quantitativement. Les autres celluloses aminées, au contraire, retiennent le bismuth moins fortement, comme on peut le remarquer à la Fig. 3 pour l'aminoéthyle à partir de laquelle le bismuth est élué avec la solution de thiocyanate (*d*), et à la Fig. 9 pour la *p*-aminobenzyle où l'élution quantitative demande de l'acide chlorhydrique 0,5*M*, c'est-à-dire à concentration nettement inférieure à celle demandée pour l'élution partielle qu'on peut obtenir sur ET et DE.

On a observé que quand l'acide nitrique était neutralisé par l'hydroxyde de bismuth, c'est-à-dire quand on utilisait la solution à grande concentration de bismuth décrite plus haut, la présence du bismuth n'était plus détectée dans les fractions d'éther de lavage (*a*) et de solution (*c*) d'élution provenant des colonnes AE, CM, P et ET. Seulement la solution concentrée de thiocyanate (*d*) et encore mieux l'acide chlorhydrique 0,5*M* pouvaient réaliser l'élution du bismuth.

Sur la base de ces résultats, on a constaté que le bismuth se sépare d'avec le mercure sur toutes les six premières celluloses, à condition de prendre un minimum d'acide nitrique quand on utilise les celluloses AE, CM, P et ET.

Ces résultats ont été étendus à la séparation d'une quantité macroscopique de

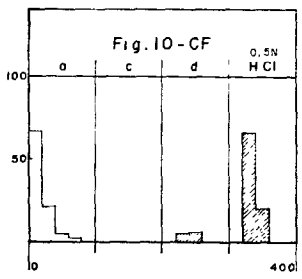


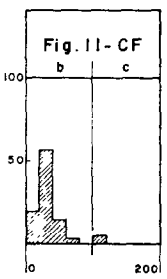
FIGS. 1–9.—Le comportement chromatographique des traces de bismuth sur celluloses et cellobiose.

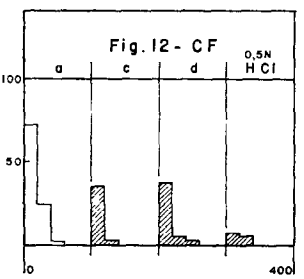
(Solution de bismuth en acide nitrique dilué en éther) Les Figs. 8 et 9 présentent aussi le comportement des traces de mercure.

bismuth d'avec des traces de mercure. Du ^{203}Hg a été additionné à la solution à haute concentration de bismuth, et la chromatographie de cette solution a été réalisée comme décrit. La séparation très nette des traces de mercure d'avec le bismuth est représentée en Fig. 10 pour la cellulose naturelle; la même Figure montre aussi comment l'adsorption du bismuth change quand l'acide nitrique est presque neutralisé (comparez Figs. 1 et 10).

La raison pour laquelle un petit pourcentage de bismuth était élué en avance par rapport à la plus grande partie de bismuth, quand l'acide nitrique n'était pas neutralisé, a été étudiée. On a remarqué que le nitrate de bismuth est très soluble dans l'acide nitrique et on a alors supposé que le responsable de l'absence d'adsorption d'une partie de bismuth était l'acide nitrique introduit dans l'éther au moment de la préparation de la solution de ^{207}Bi. Pour confirmer cette hypothèse, des colonnes de







ml effluent vs elution %

FIGS. 10.—La séparation de quelques nanogrammes de mercure d'avec 84 mg d'hydroxyde de bismuth, sur colonne de cellulose naturelle en éther éthylique.

FIG. 11.—Le comportement chromatographique de 10 mg de trichlorure de bismuth anhydre sur colonne de cellulose naturelle en éther-acide nitrique 2% [solution (*b*)].

FIG. 12.—La séparation de quelques nanogrammes de bismuth d'avec 1 g de chlorure mercurique en 20 ml d'éther éthylique, sur colonne de cellulose naturelle.

cellulose naturelle ont été préparées dans un mélange ether–acide nitrique 2% et le lavage a été effectué avec la même solution (*b*): on a constaté que le bismuth n'était plus retenu sur cellulose CF. La même chose se vérifiait quand on soumettait à la chromatographie une solution de trichlorure de bismuth dans l'éther pur: ce composé est en effet très soluble dans l'éther (Fig. 11). Il en résultait donc que la grande solubilité du nitrate de bismuth dans l'acide nitrique et du chlorure dans l'éther jouaient un rôle extrêmement important dans le phénomène d'adsorption et que les élutions pouvaient être corrigées en calculant la quantité limite d'acide nitrique dans l'éther, et en évitant le chlorure, comme on a fait.

La méthode de chromatographie sur colonnes de cellulose qui a été développée pour la purification du bismuth, se prête aussi à la purification du mercure d'avec traces de bismuth: par example 20 ml d'éther contenant un gramme de chlorure mercurique et 10 μl de solution de ^{203}Hg avec 50 μl de solution de ^{207}Bi ont été soumis à la chromatographie sur une colonne de cellulose naturelle dans l'éther et le bismuth a été séparé quantitativement d'avec le mercure. Les courbes d'élution de la Fig. 12 montrent qu'il convient d'effectuer le lavage du mercure avec 100 ml d'éther éthylique pur, et ensuite l'élution des traces de bismuth avec environ 50 ml d'acide chlorhydrique 0,5*M* dans le méthanol. Ce résultat s'ajoute à ceux qui sont déjà publiés sur la purification du mercure d'avec de nombreuses impuretés par la même méthode. La superposition de la Fig. 10 de cet article et de la Fig. 1 de la deuxième Partie de cette étude[4] permet de constater que le bismuth peut être purifié des traces de mercure et de zinc au moyen d'une seule opération, et que les trois métaux peuvent être élués sélectivement.

CONCLUSION

La conclusion immédiate de cette étude est que le bismuth et le mercure en tous les rapports de quantité peuvent être séparés réciproquement par chromatographie sur celluloses CF, DE, AE, CM, P et ET.

Si on est intéressé à la détermination des traces de mercure et de zinc dans le

bismuth, au niveau du ppm, la méthode présentée permet de recueillir les traces de mercure en solution dans l'éther: cette solution se prête bien à tous les traitements analytiques ultérieurs. La solution peut aussi être rapidement concentrée sans réchauffement et, après les traitements opportuns, être soumise à l'irradiation neutronique, pour une détermination quantitative du mercure par spectrométrie gamma. Les avantages sont la rapidité, la simplicité, les réactifs très courants et la manipulation de substances non irradiées pendant tout le cours de la séparation. Pour la détermination de traces de mercure dans le bismuth au niveau du ppb* une plus longue colonne pourrait être utilisée.

La solution qui sert à éluer le zinc peut être aussi concentrée et soumise à irradiation neutronique: elle contient en effet seulement du thiocyanate d'ammonium qui ne donne par d'interférences par activation neutronique.

Si par contre, on est intéressé à la détermination de traces de bismuth dans le mercure au niveau du ppb,* la méthode demeure valide et aussi simple que décrite. Il convient de faire le lavage du mercure avec de l'éther éthylique pur, et réaliser par la suite l'élution du bismuth avec de l'acide chlorhydrique 0,5*M* en méthanol.

Pour ce qui concerne les applications analytiques et technologiques la méthode peut être donc comparée bien favorablement avec celles qui sont disponibles.[5,6]

Le comportement des traces de bismuth en chromatographie sur celluloses dans les conditions préfixées est aussi intéressant pour plusieurs autres points de vue.

(a) Le comportement du bismuth est différent de ceux de l'arsenic et de l'antimoine et il n'y a pas d'évolution progressive avec le nombre atomique; le bismuth peut être séparé facilement d'avec l'antimoine par chromatographie sur celluloses.[3]

(b) La solubilité de certains sels se confirme être un facteur important en chromatographie sur celluloses.

(c) La purification de l'uranium d'avec des traces de bismuth sur cellulose naturelle devra se faire en conditions contrôlées, spécialement en ce qui concerne la concentration d'acide nitrique dans l'éther. Une fois que le comportement de l'uranium sur celluloses substituées sera connu, il sera éventuellement possible de réaliser la purification de l'uranium d'avec le bismuth sur l'une ou l'autre des celluloses substituées.

(d) Les celluloses aminées adsorbent le bismuth fortement et dans l'ordre suivant: DE, ET, PAB, AE. Il est intéressant de noter aussi qu'un pourcentage significatif du mercure est adsorbé sur PAB, et SE. (Figs. 8 et 9).

Chaque cellulose substituée présente une différente capacité pour la retention du bismuth, qui dépend évidemment du groupe fonctionnel. Le cellobiose donne des courbes d'élution qui ne différent pas d'une façon significative de celles de la cellulose naturelle.

Summary—The chromatographic behaviour of nanogram amounts of bismuth has been studied by radioisotope techniques on cellobiose, cellulose and seven substituted celluloses. All celluloses in ethyl ether adsorb bismuth, provided that it is as nitrate, and that excess of nitric acid is avoided. Bismuth can be eluted with thiocyanate in ether–methanol or with hydrochloric acid in methanol, depending on the retention strength of the various functional groups of celluloses. A very simple method of separation of bismuth from mercury over a wide range of concentration is presented.

* b = 10^9

Zusammenfassung—Das chromatographische Verhalten von Nanogrammengen Wismut wurde mit einer Radioisotopentechnik an Cellobiose, Cellulose und sieben substituierten Cellulosen studiert. Alle Cellulosen adsorbieren in Äthyläther als Nitrat vorliegendes Wismut, wenn ein Überschuß an Salpetersäure vermieden wird. Wismut kann mit Rhodanid in Äther-Methanol oder mit Salzsäure in Methanol eluiert werden, was vom Retentionsvermögen der verschiedenen funktionellen Gruppen abhängt. Eine sehr einfache Methode wird gezeigt, Wismut von Quecksilber in einem weiten Bereich von Konzentrationsverhältnissen zu trennen.

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CONTRIBUTIONS TO THE BASIC PROBLEMS OF COMPLEXOMETRY—XXIII*

DETERMINATION OF THORIUM, SCANDIUM AND SOME LANTHANIDES IN THE PRESENCE OF EACH OTHER

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Summary—A new method is described for the determination of thorium, scandium, and the sum of light lanthanides, in the presence of each other. The method is based on the titration of thorium plus scandium with DCTA (1,2-diaminocyclohexanetetra-acetic acid) at pH 2·5–3·5, with Xylenol Orange as indicator. After addition of TTHA (triethylenetetraminehexa-acetic acid) the thorium-DCTA complex is converted into the thorium-TTHA complex according to the equation Th-DCTA + TTHA = TH-TTHA + DCTA. Simultaneously, free lanthanum, cerium, praseodymium and neodymium react with TTHA. The excess of TTHA and the liberated DCTA are then determined by titrations with zinc and with lanthanum solutions according to the equations DCTA + TTHA + 3Zn = Zn-DCTA + Zn_2-TTHA and DCTA + TTHA + 2La = La-DCTA + La-TTHA. From the results, the amounts of thorium and scandium, and the sum of the lanthanide concentrations, can easily be calculated. Further possibilities, *e.g.*, determination of heavier lanthanides, are briefly discussed.

IN a previous paper[1] we have described consecutive titrations of thorium and lanthanum with diethylenetriaminepenta-acetic acid (DTPA) or triethylenetetraminehexa-acetic acid (TTHA). Both methods are based on the titration of thorium at pH 2·5–3·0 and of lanthanum at pH 5·0–5·5, Xylenol Orange being used as indicator. It has been claimed that such consecutive titrations cannot be performed with EDTA or 1,2-diamino-cyclohexanetetra-acetic acid (DCTA) because the thorium complexes react with the indicator above pH 4. The method with DTPA has been utilized by Gupta and Powell[2] for the determination of other rare earths. On the other hand the determination of thorium in the presence of scandium cannot be performed with an EDTA titration because their stability constants with EDTA are very close ($\log K_{ThY} = 23{\cdot}3$, $\log K_{ScY} = 23{\cdot}1$). We have found[3] that the thorium-EDTA complex reacts quantitatively with TTHA at pH 5 after short boiling, forming a thorium-TTHA complex, but the scandium-EDTA complex does not react at all. The TTHA consumed and the EDTA liberated

$$\text{Th-EDTA} + \text{TTHA} = \text{Th-TTHA} + \text{EDTA} \qquad (1)$$

can be determined by a back-titration with zinc, Xylenol Orange being used as indicator, and the amounts of thorium and scandium are easily calculated.[3]

It would be of great interest if such determinations could also be carried out in the presence of some of the lanthanides. At first we encountered some difficulties.

* Part XXII: *Talanta*, 1966, **14**, 266.

When we titrated the sum of thorium and scandium in the presence of lanthanum, the results were very good, but the subsequent determination of lanthanum with TTHA could only be performed by boiling the solution for a short time, after adding urotropine, in which case the liberated EDTA [see reaction (1)] reacted partly with the lanthanum and the reaction with TTHA was not quantitative. It seemed that such a problem could not be solved properly. Fortunately we have found that DCTA behaves differently—displaced from its thorium complex it does not react with lanthanum in the presence of TTHA. The determinations are therefore based on the following reactions.

(*a*) Determination of thorium + scandium with DCTA at pH 2·5–3·0:

$$x\text{Th} + y\text{Sc} + (x + y)\text{DCTA} = x\text{Th-DCTA} + y\text{Sc-DCTA}. \quad (2)$$

(*b*) Determination of thorium + lanthanum by reaction with an excess of TTHA at pH 5·0–5·5:

$$x\text{Th-DCTA} + z\text{La} + (x + z)\text{TTHA} = x\text{Th-TTHA} + z\text{La-TTHA} + x\text{DCTA}. \quad (3)$$

The total amount of DCTA and TTHA is known. In a mixture they can easily be determined by titrating two aliquots with lanthanum and with zinc solutions:

$$x\text{DCTA} + w\text{TTHA} + (x + 2w)\text{Zn} = x\text{Zn-DCTA} + w\text{Zn}_2\text{-TTHA} \quad (4)$$

$$x\text{DCTA} + w\text{TTHA} + (x + w)\text{La} = x\text{La-DCTA} + w\text{La-TTHA}. \quad (5)$$

EXPERIMENTAL

Reagents

DCTA, 0·05*M*, was prepared by dissolving 17·63 g of it in 150 ml of hot 1*M* sodium hydroxide. cooling, and diluting to 1 l. The solution was standardized by complexometric titration with 0·05*M* zinc solution.

TTHA, 0·05*M*, was prepared by dissolving 24·72 g of it in 150 ml of hot water, neutralizing with 1*M* sodium hydroxide, cooling, diluting to 1 l. and standardizing as above.

For preparing 0·05*M* solutions of thorium, scandium and lanthanum, the nitrates were used. Zinc solution, 0·05*M*, was prepared from metallic zinc. Solutions of other rare earths (Ce, Pr, Nd, Sm and Ho) were prepared by dissolution of their oxides in hydrochloric acid, and were 0·05*M*. The concentrations of all solutions were checked by complexometric analysis. A 0·2% Xylenol Orange solution and reagent grade urotropine were also used.

Procedure

Take two aliquots of the dissolved sample containing not more than 500 mg of thorium, scandium and lanthanide oxides, adjust both solutions to pH 2·5–3·0, add a few drops of Xylenol Orange solution, and titrate with 0·05*M* DCTA till the red colour changes to clear yellow (consumption, *a* ml). Adjust the pH to 5·0–5·5 with solid urotropine (red colour reappears), add 0·05*M* TTHA in excess—more than sufficient for thorium and lanthanum (*b* ml)—and boil the solution for 3 min. The red solution must turn yellow. Then cool and titrate one solution with 0·05*M* zinc (*c* ml) and the other with 0·05*M* lanthanum (*d* ml). The colour change of both end-points, from yellow to intense red, is very sharp. Then thorium is given by $(2d - c)$, scandium by $(a + c - 2d)$, and the lanthanide by $(b - d)$ if all the titrants are equimolar.

Some results for thorium, scandium and lanthanum are summarized in Table I and those for thorium, scandium and/or cerium, praseodymium and neodymium are included in Table II.

Remarks

In titrations with zinc solutions, the red colour at the end-point reverts after some time (5 min) to yellow, owing to the reaction:

$$\underset{\text{(red)}}{\text{La-TTHA} + \text{Zn-DCTA} + \text{ZnXO}} = \underset{\text{(yellow)}}{\text{La-DCTA} + \text{Zn}_2\text{-TTHA} + \text{XO}} \quad (6)$$

(where XO is the anion of Xylenol Orange). It is also possible to use only one aliquot if we mask all the zinc by the addition of 1,10-phenanthroline[4] after the zinc titration, and repeat the titration with lanthanum solution.

TABLE I.—DETERMINATION OF THORIUM, SCANDIUM AND LANTHANUM

Thorium			Scandium			Lanthanum		
taken, *mg*	found, *mg*	error, %	taken, *mg*	found, *mg*	error, %	taken, *mg*	found, *mg*	error, %
116·0	116·4	+0·4	$22{\cdot}4_8$	$22{\cdot}3_9$	−0·4	55·6	55·5	−0·2
	115·8	−0·2		$22{\cdot}4_6$	−0·1		55·6	0·0
58·0	58·4	+0·7	56·2	56·0	−0·4	138·9	138·8	−0·1
	58·0	0·0		56·1	−0·2		139·0	+0·1
290·1	290·1	0·0	$11{\cdot}2_4$	$11{\cdot}3_5$	+1·0	138·6	138·6	−0·0
	289·6	0·2		$11{\cdot}1_5$	−0·8		139·4	+0·2
290·1	290·2	0·0	56·2	56·3	+0·2	$27{\cdot}7_8$	$27{\cdot}7_8$	0·0
	290·9	+0·3		55·8	−0·7		$28{\cdot}3_4$	+2·0
290·1	290·3	+0·1	$11{\cdot}2_4$	$11{\cdot}2_4$	0·0	$27{\cdot}7_8$	$27{\cdot}8_9$	+0·4
	290·1	0·0		$11{\cdot}2_0$	−0·4		$28{\cdot}1_7$	+1·4
58·0	57·8	−0·3	56·2	56·4	+0·3	$27{\cdot}7_8$	$28{\cdot}0_0$	+0·8
	58·1	+0·2		56·0	−0·3		$27{\cdot}5_0$	−1·1
58·0	57·9	−0·2	$11{\cdot}2_4$	$11{\cdot}4_4$	+1·8	138·9	138·9	0·0
	57·9	−0·2		$11{\cdot}3_1$	+0·4		139·1	+0·2

TABLE II.—DETERMINATION OF THORIUM, SCANDIUM AND OTHER LANTHANIDES

Thorium			Scandium			Lanthanide		
taken, *mg*	found, *mg*	error, %	taken, *mg*	found, *mg*	error, %	taken, *mg*	found, *mg*	error, %
116·0	115·7	−0·3	$22{\cdot}4_8$	$22{\cdot}4_8$	0·0	70·0 Ce	69·6	−0·6
	116·5	+0·4		$22{\cdot}4_1$	−0·3		70·0	0·0
116·0	115·6	−0·4	$22{\cdot}4_8$	$22{\cdot}3_7$	−0·5	68·8 Pr	68·9	+0·2
	115·7	−0·3		$22{\cdot}3_7$	−0·5		68·9	+0·2
116·0	115·0	−0·9	$22{\cdot}4_8$	$22{\cdot}5_7$	+0·4	71·1 Nd	71·3	+0·3
	114·8	−1·1		$22{\cdot}7_0$	+1·0		70·7	−0·6
116·0	106·8	−8·0	$22{\cdot}4_8$	$24{\cdot}3_5$	+8·3	73·2 Sm	73·2	0·0
116·0	42·3	−63·5	$22{\cdot}4_8$	$36{\cdot}7_9$	+63·7	80·2 Ho	81·0	+1·2

DISCUSSION

The proposed method offers good results for the combination thorium, scandium, lanthanide (where lanthanide = La, Ce, Pr, Nd). Further rare earths can be determined as well, even when they do not react quantitatively according to equation (3) and are always partially bound with DCTA. In such cases their determination according to reaction (5) gives satisfactory results, but the calculation shows a negative error for the thorium and a corresponding positive error for the scandium. These errors increase with increasing stability constants of the respective lanthanide-DCTA complexes, which are responsible for the interfering reaction:

$$\text{Ln-TTHA} + \text{DCTA} = \text{Ln-DCTA} + \text{TTHA}. \qquad (7)$$

The last two results in Table II for samarium and holmium illustrate this situation quite well. The whole problem is being systematically investigated.

Zusammenfassung—Es wird eine neue Methode zur gleichzeitigen Bestimmung von Thorium, Scandium und der Summe der leichten Lanthaniden beschrieben. Die Methode beruht auf der Titration von Thorium plus Scandium mit DCTA (1,2-Diaminocyclohexantetraessigsäure) bei pH 2,5–3,5, mit Xylenolorange als Indikator. Nach Zugabe von TTHA (Triäthylentetraminhexaessigsäure) wird der Thorium-DCTA-Komplex in den Thorium-TTHA-Komplex übergeführt gemäß der Gleichung Th-DCTA + TTHA = Th-TTHA + DCTA. Gleichzeitig reagieren das freie Lanthan, Cer, Praseodym und Neodym mit TTHA. Der Überschuß an TTHA und das freigewordene DCTA werden dann durch Titration mit Zink-und mit Lanthanlösungen gemäß den Gleichungen DCTA + TTHA + 3Zn = Zn-DCTA + Zn_2TTHA und DCTA + TTHA + 2La = La-DCTA + La-TTHA bestimmt. Aus den Ergebnissen können die Thorium- und Scandiummengen sowie die Summe der Lanthanidenkonzentrationen leicht berechnet werden. Weitere Möglichkeiten, zum Beispiel die Bestimmung schwererer Lanthaniden, werden kurz diskutiert.

Résumé—On décrit une nouvelle méthode de dosage du thorium, du scandium et de la somme des lanthanides légers, en présence les uns des autres. La méthode est basée sur le dosage de thorium plus scandium au moyen de DCTA (acide 1,2-diaminocyclohexanetétracétique) à pH 2,5–3,5 avec le xylénol orangé pour indicateur. Aprés addition de TTHA (acide triéthylènetétraminohexacétique), on convertit le complexe thorium-DCTA en complexe thorium-TTHA selon l'équation Th-DCTA + TTHA = Th-TTHA + DCTA. Simultanément, les lanthane, cérium, praséodyme et néodyme libres réagissent avec le TTHA. L'excès de TTHA et le DCTA libéré sont alors dosés par titrages avec des solutions de zinc et de lanthane selon l'équation DCTA + TTHA + 3Zn = Zn-DCTA + Zn_2-TTHA et DCTA + TTHA + 2La = La-DCTA + La-TTHA. Des résultats, on peut aisément calculer les quantités de thorium et de scandium et la somme des concentrations en lanthanides. On discute brièvement d'autres possibilités, par exemple le dosage de lanthanides plus lourds.

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RADIOCHEMISCHE TRENNUNGEN MIT HILFE DER RINGOFENMETHODE—I

DAS SYSTEM $^{137}Cs/^{137m}Ba$

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Zusammenfassung—Die Anwendung der Ringofenmethode auf radiochemische Trennungen wird am Beispiel des "Mutter-Tochter"-Paares $^{137}Cs/^{137m}Ba$ erläutert. Auf Rundfiltern, welche mit schwerlöslichen Hexacyanoferraten(II) bzw. mit Salzen von Heteropolysäuren imprägniert sind, kann das ^{137m}Ba in etwa 2 min vom ^{137}Cs getrennt und nach Wiedereinstellung des radioaktiven Gleichgewichtes immer wieder "abgemolken" werden. Die erzielten ^{137m} Ba-Ausbeuten liegen bei den Hexacyanoferrat-Papieren zwischen 80 und 100%, bei den Molybdato- und Wolframatophosphat-Papieren zwischen 50 und 70%. Die Dekontaminationsfaktoren erreichen Werte von 10^3 bis 10^5. Die Halbwertszeit des abgetrennten ^{137m}Ba wurde aus den Versuchsdaten zu 2,570 ± 0,006 min errechnet.

TRENNUNGEN von Submikrogrammengen an Kationen oder Anionen lassen sich mit Hilfe der Ringofenmethode nach Weisz[1] einfach und schnell ausführen. Diese Eigenschaften sowie die Tatsache, daß die abgetrennten Substanzen an einem definierten Ort, nämlich in einem scharfen Ring von 22 mm Durchmesser, wieder konzentriert werden, haben dazu geführt, daß das Verfahren bereits verschiedentlich auf radiochemische Probleme angewendet wurde. So trennten Weisz und Scott[2] radioaktiv markiertes Sulfat, Jodid und Phosphat voneinander, während Hilton und Reed die Abtrennung von $^{137}Cs/^{137m}Ba$[3,4] sowie von $^{99}Mo/^{99m}Tc$[5] aus bestrahltem Uran beschreiben. Weiterhin wurde die Ringofentechnik zur Analyse von Gemischen langlebiger Uranspaltprodukte herangezogen.[6,7]

Von besonderem Interesse sind derartige leicht und schnell durchzuführenden Trennungen in solchen Fällen, in denen kurzlebige Radioisotopen von ihren Mutternukliden abgetrennt und identifiziert werden sollen. Hierbei ist es von Vorteil, wenn das Mutternuklid so fixiert werden kann, daß sich die "Tochter" in bestimmten Zeitabständen immer wieder "abmelken" läßt. Im folgenden wird gezeigt, wie Trennungen dieser Art beim "Mutter-Tochter"-Paar $^{137}Cs/^{137m}Ba$ bequem mit Hilfe der Ringofenmethode durchgeführt werden können.

Die Trennoperationen erfolgen auf Rundfiltern, welche mit anorganischen Ionenaustauschern, nämlich schwerlöslichen Hexacyanoferraten(II) und Salzen von Heteropolysäuren imprägniert sind. Diese Verbindungen sind dafür bekannt, daß sie bevorzugt Kationen der Ladung +1 sorbieren und eine besondere Selektivität für Cs^+ aufweisen. Als Beispiele hierfür seien einige Arbeiten aufgeführt, in welchen die selektive Sorption von Cs^+ an Kobalthexacyanoferrat(II),[8,9] Berliner Blau,[10] Vanadium(IV)-hexacyanoferrat(II),[11] Ammonium-molybdato- und wolframato-phosphat[12–14] sowie an Thallium-wolframatophosphat[15] untersucht wird bzw. radiochemisch-analytische Anwendung findet.

EXPERIMENTELLER TEIL

Herstellung der Filterpapiere

Kobalthexacyanoferrat(II)-Papiere. Rundfilter MN 2260 von 5,5 cm Durchmesser (Hersteller: Macherey, Nagel u. Co., Düren) werden mit einer 2%igen $K_4[Fe(CN)_6]\cdot 3\,H_2O$-Lösung getränkt und auf Filterpapier abgepreßt. Anschließend taucht man die Papiere 10–15 sec in eine Kobaltchlorid-Lösung, welche 0,5% Kobalt enthält, preßt sie wiederum ab und legt sie *ca.* 1 Std. in dest. Wasser, wobei dieses alle 10 min erneuert wird. Zum Schluß werden die Rundfilter mit dest. Wasser abgespült und auf Filterpapier an der Luft getrocknet.

Berliner Blau-Papiere. Die wie oben mit Kaliumhexacyanoferrat(II) imprägnierten Rundfilter werden 15–30 sec in eine salzsaure (pH ≈ 1) Eisen(III)chlorid-Lösung mit 0,5% Eisen getaucht, abgepreßt und zunächst 2 mal je 15 min in 1 n Salpetersäure gebadet. Anschließend wässert man die Papiere 1 Std. in dest. Wasser und behandelt sie weiter wie oben.

Kupferhexacyanoferrat-Papiere. Die mit einer 2%igen $K_4[Fe(CN)_6]\cdot 3\,H_2O$-Lösung getränkten Rundfilter werden 1–1½ min in eine Kupfer(II)chlorid-Lösung mit 0,5% Kupfer gelegt (Papiere dabei nicht bewegen!), abgeklatscht, 1 Std. in dest. Wasser gebadet, abgespült und an der Luft getrocknet.

Vanadiumhexacyanoferrat-Papiere. Als Reagentien dienen eine 2%ige $K_4[Fe(CN)_6]\cdot 3\,H_2O$-Lösung und eine Vanadium(IV)sulfat-Lösung mit 0,5% Vanadium. Zur Fällung werden die mit Hexacyanoferrat imprägnierten Rundfilter etwa 30 sec in die Vanadium(IV)-Lösung getaucht. Die Papiere werden weiterbehandelt wie oben.

Thalliummolybdatophosphat-Papiere. Rundfilter MN 2260 werden mit einer 4%igen Lösung von Molybdatophosphorsäure (E. Merck AG, Darmstadt) getränkt, auf Filtrierpapier abgepreßt, 15–30 sec in einer 1n salpetersauren Thalliumacetat-Lösung mit 0,5% Thallium gebadet und wiederum abgepreßt. Man legt die Papiere anschließend 10 min in 0,5n Salpetersäure, spült sie kurz mit dest. Wasser ab und läßt sie auf Filterpapier an der Luft trocknen. Die gelben Thalliummolybdatophosphat-Papiere sollten im Dunkeln aufbewahrt werden, da sie sich am Licht allmählich nach Blau verfärben.

Thalliumwolframatophosphat-Papiere. Die Imprägnierung erfolgt analog der Herstellung der Thalliummolybdatophosphat-Papiere unter Anwendung einer 4%igen Lösung von Wolframatophosphorsäure (E. Merck AG, Darmstadt).

Ammoniumwolframatophosphat-Papiere. Als Reagentien dienen eine 4%ige Wolframatophosphorsäure-Lösung und eine 1n salpetersaure 2%ige Ammoniumnitrat-Lösung. Zur Fällung werden die mit der Heteropolysäure imprägnierten Rundfilter ½–1 min in die Ammoniumnitrat-Lösung getaucht. Die Papiere werden wie oben mit 0,5n Salpetersäure und Wasser gewaschen.

Durchführung der Versuche

Die Experimente wurden mit zwei schwach salzsauren ^{137}Cs-Lösungen durchgeführt. Lösung I besaß eine spez. Aktivität von 9 μC/ml bei einer Trägerkonzentration von 0,02 mg CsCl/ml, Lösung II eine spez. Aktivität von 440 μC/ml bei einer Trägerkonzentration von 0,065 mg CsCl/ml.

Auf den Hexacyanoferrat-Papieren erfolgten die Trennungen mit 0,05n Salzsäure oder mit einer 0,05n salzsauren Bariumchlorid-Lösung mit 0,1% Barium, auf den Molybdato- und Wolframatophosphat-Papieren mit einer 0,1n salpetersauren 0,1m Ammoniumnitrat-Lösung.

Im Zentrum eines imprägnierten Rundfilters wurden 6 × 5 μl der ^{137}Cs-Lösung I (nach jeder 5 μl-Portion trocknen) oder 1 μl der Lösung II aufgetragen, sodaß sich auf dem Filter 0,27 μC bzw. 0,44 μC ^{137}Cs mit 0,6 μg bzw. 0,065 μg CsCl-Träger befanden. Auf dem Ringofen wurde dann in der üblichen Weise mit 120–150 μl der entsprechenden Waschlösung das ^{137m}Ba aus dem zentralen Cs-Tüpfelfleck abgetrennt und im Ring konzentriert. Unmittelbar nach der Trennoperation und dem Trocknen des Rundfilters wurde aus dem Zentrum desselben ein Scheibchen von 17 mm Durchmesser (mit dem Cs-Tüpfelfleck in der Mitte) herausgeschnitten (vgl. Abb. 1). Das restliche Filter mit dem im Ring konzentrierten ^{137m}Ba gelangte sofort zur Aktivitätsmessung.

Die eigentlichen Trennoperationen erforderten 2–2½ min Zeit, das Trocknen und Ausschneiden ½–1 min. Es konnte demnach etwa 2 min nach der Trennung mit der Messung begonnen werden, wenn man die Mitte zwischen Beginn und Ende des Auswaschens als den Zeitpunkt (t = 0) der Abtrennung des ^{137m}Ba vom ^{137}Cs betrachtet. Die γ-Messungen wurden mit einem NaJ(Tl)-Kristall (Frieseke u. Hoepfner, FH 421/Z 4), β-Messungen (zur Ermittlung des Dekontaminationsfaktors) mit einem Endfensterzählrohr (FHZ 15a) durchgeführt. Abbildung 2 zeigt den Abfall der Aktivität von ^{137m}Ba, welches auf Berliner Blau-Papier vom Mutternuklid ^{137}Cs abgetrennt wurde.

Aus dem 17 mm-Scheibchen mit dem Cs-Tüpfelfleck wurde 35–40 min nach der 1. Trennung ^{137m}Ba erneut "abgemolken". Hierbei wurde nach einer bereits früher beschriebenen Technik[6] das Filterscheibchen auf die Mitte eines neuen imprägnierten Rundfilters gepreßt und das ^{137m}Ba mit der geeigneten Lösung in die Ringzone gewaschen. Da hierbei Teile des ^{137}Cs (1–5% bei den

Hexacyanoferrat-Papieren, 5–10% bei den Molybdato- und Wolframatophosphat-Papieren) aus dem Filterscheibchen mit in das untere Rundfilter übergingen, mußte aus dessen Zentrum vor Beginn der Messung ebenfalls ein Scheibchen, und zwar mit 18 mm Durchmesser, ausgeschnitten werden (vgl. Abb. 1). Dieses Scheibchen enthielt die gesamte störende ^{137}Cs-Aktivität. Das "Abmelken" wurde bei jedem Versuch bis zu 3 mal durchgeführt.

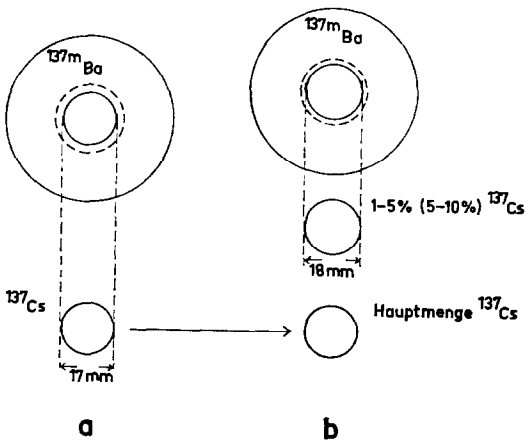

ABB. 1.—Verteilung von Mutter- und Tochternuklid auf dem Rundfilter. (a) 1. Abtrennung. (b) "Abmelken" aus dem 17mm-Scheibchen.

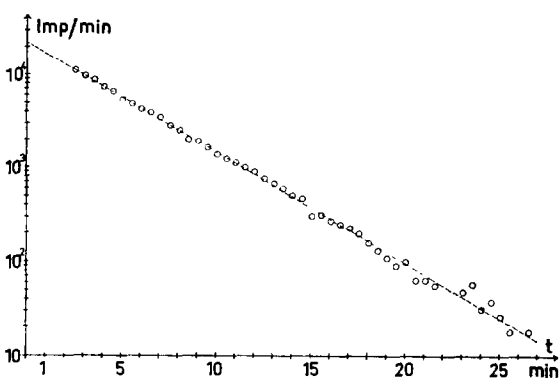

ABB. 2.—^{137m}Ba-Abfall.

ERGEBNISSE UND DISKUSSION

Als Kriterien für die Brauchbarkeit der beschriebenen Trennungen wurden die ^{137m}Ba-Ausbeute, der Dekontaminationsfaktor und die Halbwertszeit des abgetrennten ^{137m}Ba herangezogen.

Die Ausbeute wurde aus der auf den Zeitpunkt $t = 0$ extrapolierten Anfangsaktivität des ^{137m}Ba ermittelt, der Dekontaminationsfaktor durch β-Messung von Filterscheibchen und Ring (etwa 35 min nach der Trennung) und die Halbwertszeit rein rechnerisch nach der auf kurzlebige Strahler mit Vorteil anwendbaren sog. "Quotientenmethode" (vgl. z.B. bei G. Böhler[16]). Bei diesem Verfahren benötigt man als bekannte Größen nur die Impulszahl zu einem bestimmten Zeitpunkt t nach Beginn der Messung (im vorliegenden Fall nach 3 min), die Gesamtimpulszahl bis

zum völligen Abklingen der Aktivität (im vorliegenden Fall nach 35 min) und die Nullrate.

Es zeigte sich, daß man auf den Hexacyanoferrat-Papieren ^{137m}Ba-Ausbeuten zwischen 80 und 100% erreicht, wenn man die Trennungen mit der 0,05n salzsauren Bariumchlorid-Lösung durchführt. Arbeitet man mit 0,05n Salzsäure allein, trennt man also praktisch trägerfrei, dann erzielt man die gleichen Ausbeuten nur auf den Berliner Blau-Papieren. Die Dekontaminationsfaktoren liegen im allgemeinen bei den 1. Abtrennungen zwischen $5 \cdot 10^2$ und 10^3, beim folgenden "Abmelken" aus den 17 mm-Scheibchen jedoch zwischen 10^3 und 10^5.

Ähnlich lagen die Verhältnisse bei der Untersuchung der Thallium- und Ammoniumwolframatophosphat-Papiere. Die ^{137m}Ba-Ausbeuten beim "Abmelken" aus den 17mm-Scheibchen erreichten jedoch nur 50–70%. Als weniger brauchbar für ^{137}Cs-^{137m}Ba-Trennungen erwiesen sich die Thalliummolybdatophosphat-Papiere, da hiermit bei zwar hohen Ausbeuten stets nur Dekontaminationsfaktoren $<10^3$ erreicht werden konnten. Berechnungen der Halbwertszeit von ^{137m}Ba nach der erwähnten "Quotientenmethode" wurden nur bei denjenigen Versuchen durchgeführt, bei denen das Tochternuklid mit Dekontaminationsfaktoren $>10^3$ vom Mutternuklid abgetrennt werden konnte.

Folgende Ergebnisse wurden gefunden:

2,581 ± 0,014 min	2,557 ± 0,008 min
2,556 ± 0,012 min	2,573 ± 0,015 min
2,585 ± 0,017 min	2,563 ± 0,011 min
2,577 ± 0,015 min	2,574 ± 0,009 min
2,522 ± 0,022 min	2,578 ± 0,011 min
2,589 ± 0,012 min	2,559 ± 0,015 min
2,539 ± 0,014 min	2,574 ± 0,006 min
2,627 ± 0,012 min	2,549 ± 0,008 min
2,629 ± 0,013 min	2,530 ± 0,006 min
2,579 ± 0,007 min	2,552 ± 0,007 min

Aus diesen 20 Ergebnissen ließ sich für die Halbwertszeit von ^{137m}Ba der Mittelwert 2,570 ± 0,006 min errechnen, der eine gute Übereinstimmung mit dem genauesten bisher bekannten Wert von 2,554 ± 0,003 min[8] aufweist. Das geschilderte Verfahren zeigt, wie mit Hilfe der Ringofenmethode radiochemische Trennungen schnell und einfach durchgeführt werden können. Hierbei soll das System ^{137}Cs/^{137m}Ba nur als Beispiel für weitere "Mutter-Tochter"-Paare oder Nuklidgemische dienen. Auch dann, wenn im Hinblick auf die Halbwertszeit der abgetrennten Isotopen schnelle Trennungen nicht unbedingt erforderlich sind, dürfte die angegebene Arbeitsweise von Vorteil sein. Man führt alle Operationen auf einem festen Trägermaterial aus und hat die getrennten Nuklide stets in einer definierten Geometrie (zentraler Tüpfelfleck bzw. Ringzone) vorliegen.

Summary—The application of the ring-oven method to radiochemical separations is exemplified by separation of the mother-daughter pair ^{137}Cs/^{137m}Ba. The ^{137m}Ba can be separated from ^{137}Cs in about 2 min on a filter circle impregnated with an insoluble ferrocyanide or heteropoly acid salt, and after re-establishment of radioactive equilibrium can be "milked off" again. The yield of ^{137m}Ba obtained is 80–100% for the ferrocyanide-impregnated paper and 50–70% for a paper impregnated with a phosphomolybdate or tungstomolybdate. The decontamination factor ranges from 10^3 to 10^5. The half-life of the separated ^{137m}Ba was calculated to be 2.570 ± 0.006 min.

Résumé—L'application de la méthode du four annulaire aux séparations radiochimiques est illustrée par la séparation de la paire de filiation $^{137}Cs/^{137m}Ba$. On peut séparer le ^{137m}Ba du ^{137}Cs en 2 mn environ sur un cercle de papier filtre imprégné par un ferrocyanure insoluble ou par un sel d'hétéropolyacide et, après rétablissement de l'équilibre radioactif, traiter de nouveau. Le rendement obtenu en ^{137m}Ba est de 80–100%, pour le papier imprégné de ferrocyanure, et de 50–70% pour un papier imprégné de phosphomolybdate ou de tungstomolybdate. Le facteur de décontamination va de 10^3 à 10^5. On a calculé que la période du ^{137m}Ba séparé est de 2,570 ± 0,006 mn.

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RADIOCHEMICAL SEPARATION OF LEAD BY AMALGAM EXCHANGE

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Summary—An amalgam exchange technique has been used for the rapid radiochemical separation of lead. A number of variables which affect the exchange were studied and a lead yield of 88·5% was obtained. At room temperature the procedure requires about 13 min, whereas at 40° it can be completed in about 9 min. Radioactive tracers of 16 different elements were used to check the selectivity of this procedure, which has also been applied for the separation of ^{212}Pb from thorium nitrate solution.

PREVIOUS work on isotopic exchange between a dilute amalgam of a metal and its ions in aqueous solution has proved very useful for radiochemical separations of cadmium,[1] indium,[2] strontium,[3] bismuth,[4] and thallium.[5] In the amalgam exchange technique, a simple procedure gives excellent decontamination which is much better than that obtained previously. These studies show that the heterogeneous isotopic exchange reactions are rapid and selective and can be employed for rapid radiochemical separations. A preliminary communication[6] indicated that the amalgam exchange technique can also be applied to the radiochemical separation of lead. The aim of the present investigation is to develop an optimum procedure for the separation of radio-lead by this technique.

The separation is carried out in two steps. In the first step a dilute lead amalgam is made to contact an aqueous solution containing radioactive isotopes of lead, in order to selectively exchange radioactive lead with the inactive lead in the amalgam. The exchange reaction may be represented by

$$Pb(Hg) + \overset{*}{Pb}^{2+} \rightleftharpoons \overset{*}{Pb}(Hg) + Pb^{2+}$$

where the asterisk denotes radioisotopes of lead. In the second step the amalgam containing radio-lead is removed and contacted with a solution of copper(II) nitrate or lead nitrate to strip the element from the mercury into the aqueous phase.

EXPERIMENTAL

Apparatus

The separations were made in one-ounce square-bottomed flint glass bottles with polyethylene insert caps. The bottles were clamped in a mechanical shaker (Wrist-Action shaker, Burrell Corp., Pittsburg, Pa., U.S.A.), to which an extension arm of 9 in. was connected to give additional radial action. For high temperature studies the bottles were agitated in a thermostatically controlled tank.

Gross gamma ray measurements were made with a Baird Atomic Model 810 scintillation well counter, and gamma ray spectrum measurements with a 3 in. × 3 in. NaI(Tl) crystal coupled with a Nuclear Data 512 channel analyser. A Tracerlab Geiger tube TGC-1 was used for beta activity measurements.

Reagents

Mercury: triply distilled, CENCO, U.S.A., further purified by washing with dilute nitric acid, followed by rinsing with distilled water.

Lead metal: C.P., City Chemical Co., New York, U.S.A.

Thorium nitrate: Reagent grade, May & Baker Ltd., England.

All radioisotopes used as tracers were obtained from the Radiochemical Centre, Amersham, England and from the Union Carbide Nuclear Company, Oak Ridge, Tenn., U.S.A.

The lead-212 tracer was prepared from thorium in equilibrium with its decay products, by adsorbing the lead, bismuth, thallium and polonium on a column of De-Acidite FF (100–200 mesh) anion-exchange resin. After the column had been washed with 2*M* hydrochloric acid, the lead-212 was eluted with distilled water.[7]

Preparation of lead amalgam

The lead metal was washed with 2*M* nitric acid until etched, washed with distilled water and dried. The appropriate weight of lead was added to 20 g of purified mercury stored under 0·1*M* nitric acid, heated and stirred.

Exchange procedure

Lead-212 tracer was added to 4 ml of 1*M* hydrochloric acid solution for yield determination and interference studies. Radioactive tracers (10^5–10^6 cpm) of contaminating ions plus 1 μg of inactive lead were used for decontamination studies. Lead amalgam (200 μl $\sim$ 2·6 g) containing 2% lead by weight was added and the mixture was mechanically agitated for 3 min. A 200 μl aliquot was removed for counting and the aqueous phase was removed by suction. The amalgam was transferred to another bottle and washed twice with distilled water. The amalgam was then transferred to a bottle containing 2 ml of copper(II) nitrate solution in 1*M* nitric acid (25 mg of copper per ml) and agitated for 8 min. A 500 μl aliquot of the aqueous layer containing the separated lead isotopes was counted in a scintillation well-counter. The procedure requires about 13 min at room temperature and gives a yield of about 88·5%.

Separation of lead-212 from thorium nitrate

Lead amalgam (2%, 200 μl) was added to 5 ml of 50% thorium nitrate solution in 1*M* hydrochloric acid and agitated for 2 min at 40°. The aqueous layer was removed by suction and the amalgam was transferred to another bottle and washed twice with distilled water. The amalgam was then mixed with 2 ml of lead nitrate solution in 1*M* nitric acid (100 mg of lead per ml) and agitated for 5 min at 40°. The solution containing separated lead-212 was transferred to a new bottle and 10 μg of thallium carrier were added. Then 200 μl of 2% thallium amalgam were added and the mixture agitated for one min at 40° to remove thallium from the solution. Total time of separation is about 12 min, and a yield of about 66% is obtained.

DISCUSSION AND RESULTS

In the search for a suitable exchange medium, the amalgam was agitated in various systems. In general, the acid media were found to permit maximum exchange. With 2% lead amalgam and a 3-min contact time exchange yields of 93·2%, 90·1% and 86·3% were obtained for 1*M* solutions of hydrochloric acid, hydrobromic acid and nitric acid. When the amalgam was agitated in 1*M* sulphuric acid, a white turbidity due to the formation of lead sulphate was observed. Further experiments with different concentrations of hydrochloric acid showed that maximum exchange is obtained in 0·7–1·5*M* hydrochloric acid media, and 1*M* hydrochloric was therefore selected as the exchange medium.

In order to determine the optimum separation procedure several preliminary experiments were performed in which a number of factors which affect the exchange such as the concentration of lead in the amalgam and in the aqueous phase, the agitation time and the effect of temperature were studied and optimized.

As the amount of lead in the amalgam was gradually increased from 0·1 to 2% the exchange yield rapidly increased from 58·5% to 93·2%. Further increase in the concentration of lead amalgam did not show any significant increase in the yield. Studies made with different volumes of a 2% lead amalgam gave the best yields with 200 μl portions of the amalgam.

Because for high exchange it is necessary that the concentration of lead in the amalgam should be much greater than its concentration in the aqueous phase,

experiments were carried out to determine the maximum usable aqueous concentration of lead. In these experiments the aqueous concentration of lead was varied, the lead concentration in the amalgam being kept at 2%. It was found that above an aqueous concentration of 125 μg of lead per ml the exchange starts decreasing. Further studies showed that the exchange decreased if more than 5 ml of aqueous phase were used, and the optimum ratio of the volumes of aqueous phase and amalgam is 25.

The exchange yield depends upon the duration of agitation, increases rapidly with increasing agitation time and begins to level off at 3–4 min. On prolonged agitation, the exchange gradually decreases, probably because of oxidation of lead from the amalgam by air trapped in the bottle above the solution. The results are shown in Table I.

TABLE I.—DEPENDENCE OF LEAD YIELD ON AGITATION TIME AND TEMPERATURE*

Agitation time, *min*	Initial exchange, %		Back-exchange in copper nitrate system, %		Back-exchange in lead nitrate system, %	
	24°C	40°C	24°C	40°C	24°C	40°C
1	54·8	92·4	—	81·4	—	38·8
2	85·5	96·8	69·7	94·6	42·6	50·4
3	93·2	97·9	80·3	96·8	50·8	61·5
4	96·4	97·6	—	—	—	—
5	97·8	96·8	88·5	98·3	65·3	72
6	96·9	—	—	—	—	—
7	—	—	93·1	98·4	70·6	—
8	96·4	96·2	95·0	—	71·0	72
10	96	—	96·0	—	72·0	—

* In these experiments 200 μl of 2% lead amalgam were used. The back-extracting solutions contained 25 mg of copper or 100 mg of lead per ml.

In the initial exchange most of the radioactivity is transferred to the amalgam in a short time. The next step is then to reclaim this activity from the amalgam into an aqueous solution by selectively stripping the element. Of the several solutions tried for back-exchange, only lead nitrate and copper nitrate solutions in 1*M* nitric acid were efficient. The back-exchange increases with increasing concentrations of lead and copper in the solutions and above a certain concentration no more increase is observed. Therefore, solutions containing 100 mg of lead or 25 mg of copper per ml of 1*M* nitric acid were chosen as back-extractants. With 8-min agitation back-exchange yields of 72% and 95% respectively were obtained when lead nitrate and copper nitrate were used.

The dependence of back-exchange yield on the duration of agitation is shown in Table I. With increasing agitation time the yield increases and starts leveling off at 7–8 min agitation. Therefore, in the optimum separation procedure a 3-min agitation for the initial exchange and an 8-min agitation for the back-exchange were used.

Both the initial and the back-exchange reactions were studied at 40°. The results are given in Table I. The exchange reactions proceed somewhat faster at high temperature and a relatively shorter time is required to attain equilibrium. Thus at 40° the agitation times for the initial and the back-exchange can be reduced to 2 and 5 min respectively.

In the interference studies it was found that the exchange yield is not affected by

alkalies in concentrations up to 1*M*. Acids such as sulphuric, phosphoric and oxalic below 0·1*M* concentrations do not interfere whereas sulphites and oxidizing agents do interfere in the exchange. It is therefore necessary that the oxidizing agents should be reduced to their lowest oxidation state before the amalgam exchange.

Decontamination

The selectivity of this method was checked by making decontamination studies with radioactive tracers of a number of elements representative of the periodic table. The results are summarized in Table II. The elements have been listed in the order

TABLE II.—SEPARATION OF LEAD AND CONTAMINANTS*

Tracer	Weight† μg	Electrode potential‡ *V*	Separation, %		Total separated, %
			Exchange step	Back-extraction step	
^{131}I	C.F.	¶	0·018	—	<0·014
^{137}Cs	2·1	−2·92	0·01	—	<0·02
^{140}Ba–^{140}La	C.F.	−2·9, −2·52	0·003	—	<0·005
^{90}Sr–^{90}Y	C.F.	−2·89, −2·34	0·001	—	<0·001
^{144}Ce–^{144}Pr	13	−2·48, −2·47	0·005	—	<0·003
^{95}Zr–^{95}Nb	C.F.	−1·53, −1·1	0·15	—	<0·001
^{65}Zn	C.F.	−0·76	0·05	57·1	0·031
^{115m}Cd	C.F.	−0·40	2·1	0·02	<0·001
^{204}Tl	1·4	−0·34	4·4	68	3
^{60}Co	0·3	−0·28	0·036	—	<0·013
^{212}Pb	C.F.	−0·28	93·2	95	88·5
^{124}Sb	1·6	+0·21	0·98	2·91	0·03
^{207}Bi	C.F.	+0·32	95	84·2	80
^{207}Bi	C.F.	+0·32	95	0·001	<0·001
^{106}Ru–^{106}Rh	1·3	+0·61, +0·25	1·15	1·1	0·013
^{192}Ir	C.F.	+0·77	28·6	0·84	0·024
^{203}Hg	16·1	+0·79	24·4	0·41	0·05
^{110m}Ag	0·6	+0·80	77·8	0·047	0·035

* Average of duplicate runs. Lead is average of 7 runs, standard deviation 1·9%.
† Weight of inactive element present before separation. C.F. = carrier-free.
‡ Standard electrode potential for lowest stable oxidation state. Data taken from Latimer.[8]
¶ Iodine in its lowest reduced state.

of their reduction potentials and the data have been subdivided to show the selectivity in the amalgam exchange step and in the back-extraction step. It is observed that the elements above lead (in Table II), with the exception of thallium and cadmium, do not contaminate the initial exchange step within the sensitivity of the experiments *i.e.*, with the amount of tracer used (10^5–10^6 cpm), whereas the other elements do contaminate the initial exchange step, probably because their ions are reduced by lead amalgam. With the exception of bismuth these activities remain in the amalgam and are not extracted when copper(II) nitrate solution is used for selective removal of lead from the amalgam. Bismuth, however, is extracted together with lead and causes considerable contamination. Several unsuccessful attempts were made to reduce this contamination by bismuth. It was finally reduced to less than 0·001% when lead nitrate solution was used for back-extraction; this exchanges with the lead without oxidizing bismuth from the amalgam. Although the back-exchange yield is only 72% with lead nitrate solution, it gives very good separation of lead from bismuth.

The simple amalgam exchange procedure was applied to the separation of lead-212 from thorium nitrate. The gamma-ray spectrum of the separated sample showed only about 3% contamination by thallium-208. To reduce this contamination an additional step was added. The separated sample was agitated with a 2% thallium amalgam for 1–2 min to exchange thallium selectively from the solution. By this treatment the contamination by thallium was reduced to less than 1%.

The amalgam exchange technique for the radiochemical separation of lead is simple and rapid and appears to have useful potential for the separation of short-lived isotopes of lead. The yield can be further increased by shaking longer, and the time of separation can be reduced by performing the exchange at high temperatures. Although very small amounts of lead can be separated by this technique, the final sample counted contains a large amount of inactive lead, and self-absorption corrections may be necessary if beta-counting is used.

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Zusammenfassung—Ein Amalgam-Austauschverfahren wurde zur schnellen radiochemischen Abtrennung von Blei benutzt. Eine Anzahl Variabler, die den Austausch beeinflussen, wurde studiert und eine Bleiausbeute von 88,5% erzielt. Bei Zimmertemperatur dauert das Verfahren etwa 13 min, während es bei 40° in etwa 9 min beendigt werden kann. Radioaktive Tracer von 16 verschiedenen Elementen wurden benutzt, um die Selektivität des Verfahrens zu prüfen, das auch zur Abtrennung von ^{212}Pb aus Thoriumnitratlösung angewandt wurde.

Résumé—On a utilisé une technique d'échange par amalgame pour la séparation radiochimique rapide du plomb. On a étudié un certain nombre de variables qui affectent l'échange et obtenu un rendement en plomb de 88,5%. A température ordinaire, la technique nécessite environ 13 mn, alors qu'à 40° elle peut être réalisée en 9 mn environ. On a utilisé les traceurs radioactifs de 16 éléments différents pour vérifier la sélectivité de cette méthode, qu'on a aussi appliquée à la séparation du ^{212}Pb d'une solution de nitrate de thorium.

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THE REACTION OF URANYL IONS WITH 4-(2-PYRIDYLAZO)RESORCINOL

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Summary—The uranyl ion and 4-(2-pyridylazo)resorcinol (PAR) form only 1:1 chelates in solutions of pH < 8·5, $UO_2(PAR)H^+$ being formed at pH > 3 and $UO_2(PAR)$ at pH > 5·5. Equilibrium constants and spectrophotometric data for both chelates are given. Solid, non-stoichiometric crystalline species in which the mole ratio of PAR to uranium is more than 1:1 are precipitated up to pH 6. The medium of 0·1–0·2*M* triethanolamine at pH 8 recommended by other workers proved satisfactory for the sensitive spectrophotometric determination of uranium, as did pH 3·6 in the presence of < 0·1*M* formate or 20–30% v/v dimethylformamide.

4-(2-PYRIDYLAZO)RESORCINOL (PAR) has been shown to be a sensitive reagent for uranium, and several methods for the spectrophotometric determination of uranium at pH 7–8 have been proposed.[1–3] However, there is disagreement concerning the complexation equilibria. Geary *et al.*,[1] from their potentiometric studies, proposed the formation of a 1:2-chelate at pH 8. Others have assumed a 1:1 species in alkaline medium.[2,3] Because the resolution of these differences is of particular interest for practical spectrophotometry the complexation of the uranium ion with PAR was studied anew by suitable spectrophotometric methods.

EXPERIMENTAL

The preparation of solutions of uranium, the experimental conditions and the apparatus used have been described previously;[4] only reagents not described earlier are listed below.

Reagents

4-(2-Pyridylazo)resorcinol (PAR). Samples used were products of Lachema, Brno or Chemapol, Prague. The purity was always checked by descending paper chromatography with methanol–acetic acid–water (6:3:1), n-butanol–ammonia–water (5:1:5) or pyridine–pentanol–ammonia (5:5:1) on Whatman No. 1 or No. 4 paper, by elemental analysis, and by titration with chromous chloride.[4] The content of the active dye was never lower than 85%. The calculated amounts were dissolved in water or dimethylformamide. The ionic strength was usually adjusted to 0·1, and the pH was regulated by addition of 0·1 and 0·5*M* sodium hydroxide, ammonia or perchloric acid. In special cases buffers were used, *e.g.*, 0·1*M* triethanolamine (pH 8 and 7·7) or 0·1*M* tris(hydroxymethyl)aminomethane (pH 8·05).

Spectrophotometric methods used for solutions

The complexation equilibria, the composition and the molar absorptivities of the chelates were studied by the various spectrophotometric methods used previously.[4–6]

RESULTS AND DISCUSSION

Acid-base equilibria of PAR

The concentrations of the ligand species present in solution (H_3R^+, H_2R, HR^- and R^{2-}) are determined by the acid dissociation constants, $pK_{a1} = 3{\cdot}1$ (2·64), $pK_{a2} =$

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5·6 (5·9), $pK_{a3} = 11·9$ where the figures in brackets are for 30% v/v dimethylformamide media.[9] Only the first three proved to be important. The molar absorptivities of H_3R^+, H_2R and HR^- respectively, at 510 mμ and (in brackets) at 470 mμ, are $3·7 \times 10^3$ ($1·84 \times 10^4$), $2·5 \times 10^3$ ($1·95 \times 10^4$) and $7·8 \times 10^2$. The absorption maxima in water, 30% v/v dimethylformamide and 90% dimethylformamide occur at 395, 430–444 and 441–8 mμ respectively for H_3R^+; 385, 388 and 389 mμ for H_2R; and 413, 413 and 394 mμ for HR^-.

Reaction with uranyl ions

PAR-solutions turn orange or dark red at pH > 3 in the presence of uranyl ions. At pH 4·5–6 the chelate formed partly precipitates or forms colloidal solutions, especially when excess of ligand is present, but at pH > 6 the solutions are clear. However, a red-violet solid layer floats on the surface of the liquid and can only be dissolved by addition of ethanol or dimethylformamide. The sensitivity is pD = 7·0 at pH 5–6 (pD = −log [dilution limit]) referred to 1 ml of solution. Uranium(IV) reacts similarly at pH > 4·5.

Spectra of the uranyl chelate solutions

The spectra of the uranyl chelates were measured for solutions containing various concentrations of components and at different pH so that in turn H_3R^+ (λ_{max} 395 mμ), H_2R (λ_{max} 385 mμ) or HR^- (λ_{max} 413 mμ) were co-ordinated (Fig. 1). Some experimental results are given in Table I.

TABLE I.—WAVELENGTH MAXIMA AND ISOSBESTIC POINTS FOR URANIUM(VI)-PAR

pH	C_M, M	C_R, M	λ_{max}, mμ	Isosbestic point, mμ
1·8–3·3	$5·37 \times 10^{-3}$	$5·55 \times 10^{-5}$	500	470
33·2–10·2	$3·38 \times 10^{-5}$	$3·38 \times 10^{-5}$	525	460
6·45–10·5	$1·35 \times 10^{-5}$	$6·76 \times 10^{-5}$	525–30	455
7·68	$(1·0–7·5) \times 10^{-5}$	$1·25 \times 10^{-4}$	525	455
2·14–3·14	$1·0 \times 10^{-3}$	$5·0 \times 10^{-5}$	500*	473

* 4% v/v dimethylformamide.

The interference of the protonated form H_3R^+ shifts the absorbance curves for solutions with metal ion excess from the isosbestic point, at pH < 1·8. The curves have a deformed maximum or inflexion point of lower intensity belonging to the H_2R-form of the ligand at 390–400 mμ besides the regular chelate maximum at 500 mμ, even when the chelate is quantitatively formed at pH > 3. This was explained earlier by the formation of a protonated MRH-chelate where the *p*-hydroxy proton is not dissociated.[9] These two different species have absorption maxima at 510 and 526–535 mμ respectively in 30% v/v dimethylformamide.

pH–Absorbance curves and their interpretation

Solutions with excess of metal ion. S-shaped curves with a straight line portion between pH 1·90 and 2·93 when $C_R = 5 \times 10^{-5} M$ and $C_M/C_R = 20–100$ are characteristic of a single chelate equilibrium. The chelate formation is evidently shifted to

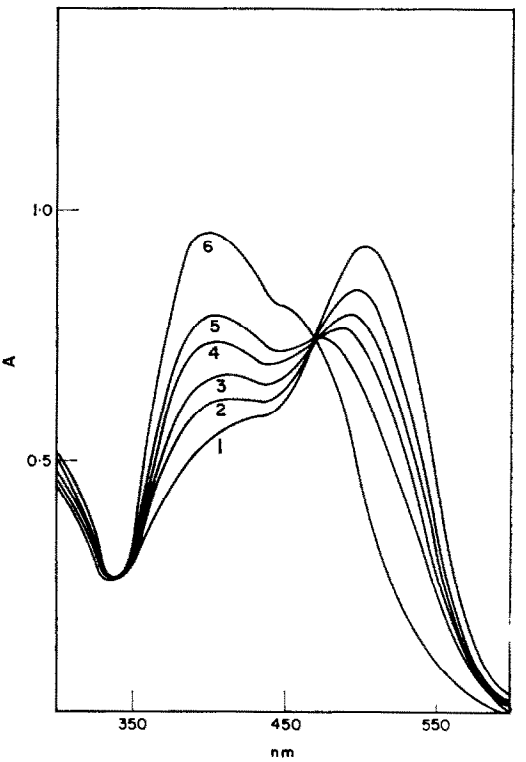

FIG. 1(a).—Absorption curves of PAR solutions in the presence of excess of uranium(VI).
$C_M = 5{\cdot}368 \times 10^{-5}M$; $C_R = 5{\cdot}55 \times 10^{-5}M$; pH: *1*—3·27; *2*—2·98; *3*—2·70; *4*—2·53; *5*—2·41; *6*—1·84.

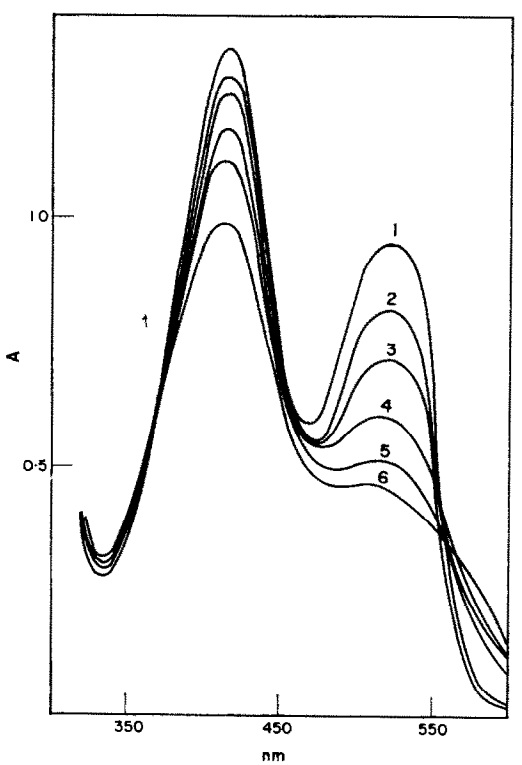

FIG. 1(b).—Absorption curves of uranyl(VI) solutions in the presence of excess of PAR.
$C_R = 6{\cdot}76 \times 10^{-5}M$, $C_M = 1{\cdot}352 \times 10^{-5}M$; pH: *1*—8·10; *2*—9·00; *3*—6·73; *4*—6·45; *5*—6·20; *6*—6·05.

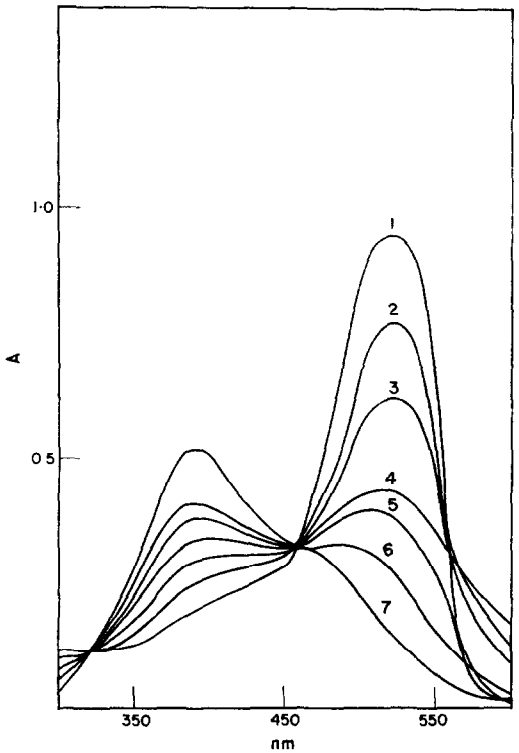

FIG. 1(c).—Absorption curves of equimolar solutions of uranyl(VI) and PAR. $C_R = C_M = 3{\cdot}38 \times 10^{-5}M$; pH: *1*—7·38; *2*—6·81; *3*—6·23; *4*—5·85; *5*—4·57; *6*—3·76; *7*—3·21.

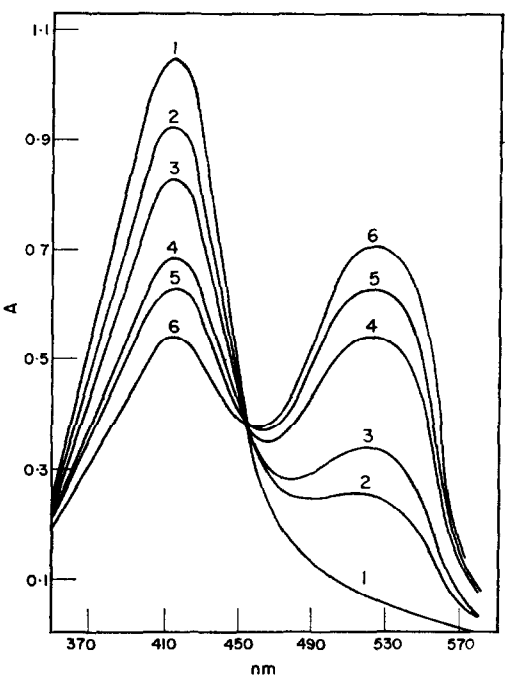

FIG. 1(d).—Absorption curves of PAR solutions with increasing uranyl(VI) concentrations at pH 7·68 (0·5-cm cells). $C_R = 1{\cdot}25 \times 10^{-4}M$. *1*—PAR only; *2*—$C_M = 1{\cdot}10^{-5}M$; *3*—$C_M = 1{\cdot}5 \times 10^{-5}M$; *4*—$C_M = 2{\cdot}5 \times 10^{-5}M$; *5*—$C_M = 3{\cdot}0 \times 10^{-5}M$; *6*—$C_M = 7{\cdot}5 \times 10^{-5}M$.

lower pH values with the increasing metal ion or ligand concentration (Fig. 2). The following equilibria were examined to see if they explained the chelation at pH < 3:

$$UO_2^{2+} + H_3R^+ \rightleftharpoons UO_2RH^+ + 2H^+ \quad (A)$$

$$UO_2^{2+} + H_2R \rightleftharpoons UO_2RH^+ + H^+. \quad (B)$$

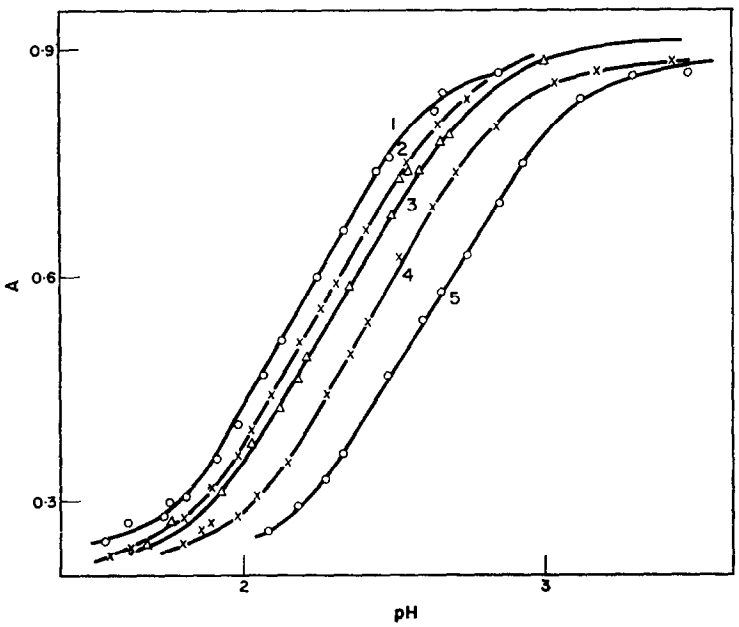

FIG. 2.—Absorbance-pH plots for PAR solutions with increasing uranyl(VI) concentrations at 510 mμ.
$C_R = 5{\cdot}10^{-5}M$, C_M: *1*—$5 \times 10^{-5}M$; *2*—$4 \times 10^{-5}M$; *3*—$3 \times 10^{-5}M$; *4*—$2 \times 10^{-5}M$; *5*—$1 \times 10^{-5}M$.

The following basic equations are valid for the interpretations of the ascending part of the curves, taking into account the partial dissociation of the ligand.

$$C_M \sim [M]$$

$$C_R = [MRH] + [H_3R](1 + K_{a1}/[H]) \text{ or } [MRH] + [H_2R](1 + [H]/K_{a1})$$

$$A = \varepsilon_{1H}[MRH] + [H_3R](\varepsilon_{R1} + \varepsilon_{R2}K_{a1}/[H]) \text{ or}$$

$$\varepsilon_{1H}[MRH] + [H_2R](\varepsilon_{R1}[H]/K_{a1} + \varepsilon_{R2})$$

$$A_{0R} = \varepsilon_{R1}C_R + \varepsilon_{R2}C_RK_{a1}/[H] \text{ for equilibrium (A) and}$$

$$\varepsilon_{R2}C_R + \varepsilon_{R1}C_R[H]/K_{a1} \text{ for equilibrium (B)}$$

$$A_{01} = \varepsilon_{1H}C_R$$

$$k_{12} = [MRH][H]^2/[M][H_3R] \text{ for equilibrium (A) and}$$

$$k_{11} = [MRH][H]/[M][H_2R] \text{ for equilibrium (B).}$$

$$C_R/A = \frac{1}{\varepsilon_{1H}} + \frac{\{A(1 + K_{a1}/[H]) - A_{0R}\}[H]^2}{Ak_{12}\varepsilon_{1H}C_M} \quad (1)$$

for equilibrium (A) and

$$C_R/A = \frac{1}{\varepsilon_{1H}} + \frac{\{A(1 + [H]/K_{a1}) - A_{0R}\}[H]}{Ak_{11}\varepsilon_{1H}C_M} \tag{2}$$

for equilibrium (B).

Similarly, for equilibrium (A) and (B) respectively, we have

$$\log\left\{\frac{A(1 + K_{a1}/[H] - A_{0R}}{A_{01} - A}\right\} = \log C_M + \log k_{12} + 2pH \tag{3}$$

and

$$\log\left\{\frac{A(1 + [H]/K_{a1}) - A_{0R}}{A_{01} - A}\right\} = \log C_M + \log k_{11} + pH \tag{4}$$

where ε is the molar absorptivity of the species indicated by the subscript (1H = MRH; R1 = H_3R^+, R2 = H_2R). Charges are omitted. The existence of equilibria

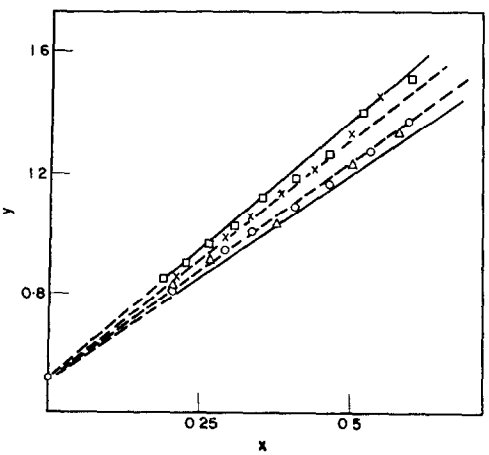

FIG. 3.—Analysis of the linear portions of the pH-absorbance plots, according to equation (1).

$$x = \frac{\{A(1 + K_{a1}/[H]) - A_{0R}\}[H]^2 \times 10^{-3}}{A}; \quad y = \frac{C_R \times 10^{-5}}{A - A_{0R}}.$$

$C_R = 5 \times 10^{-5}M$; C_M/C_R: $\Delta = 100$; $\circ = 60$; $\times = 40$; $\square = 20$; 510 mμ.

(A) and (B) was confirmed by the linearity of transformations (1) and (2). Equilibrium (A) predominates between pH 2 and 2·6 for $C_M/C_R = 20$–100. The number of protons lost during chelation was also confirmed by application of equations (3) and (4) (Figs. 3 and 4). The pH curves show the influence of hydrolysis at pH > 3·5. Further complex formation for solutions containing a small metal ion excess takes place at pH 4–5·5 in the presence of 30% v/v dimethylformamide, but the details of the equilibrium are not given here. The mononuclear character of the 1:1-complex formed at pH < 3 was proved by the linearity of transformation (5), derived from (1):

$$\frac{C_R}{A - A_{0R}} = \frac{1}{\varepsilon_{1H} - \bar{\varepsilon}_R} + \frac{1}{\gamma_1(\varepsilon_{1H} - \bar{\varepsilon}_R)\{C_M - m(A - A_{0R})/(\varepsilon_{1H} - \bar{\varepsilon}_R)\}^m} \tag{5}$$

where m is the number of metal ions in the complex, $\bar{\varepsilon}_R$ is the apparent molar absorptivity for the ligand irrespective of the species present, and γ_1 is the apparent stability

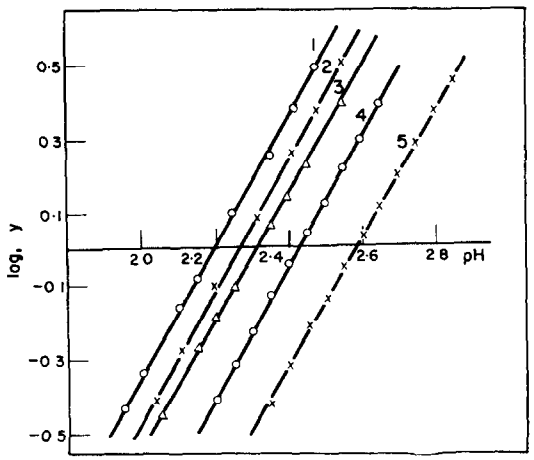

FIG. 4.—Logarithmic plots according to equation (3).

$y = \log \dfrac{A(1 + K_{a1}/[H]) - A_{0R}}{A_{01} - A}$. Working conditions as in Fig. 3.

constant for MRH. The plot $C_R/(A - A_{01}) = f(1/C_M)^m$ was only linear when $m = 1$, pH = 2·1, $C_R = 1{\cdot}22 \times 10^{-4}M$ and $C_M = 10^{-3}$–$10^{-2{\cdot}3}M$. From the value of ε_{1H} determined from equation (5), m can be calculated by means of equation (6):

$$\log \frac{A(1 + K_{a1}/[H] - A_{0R}}{A_{01} - A} = m \log C_M + \log \gamma_1. \qquad (6)$$

The value of m obtained was 0·8 (Fig. 5) and this shows that oligonuclear complexes are not formed in this pH region.

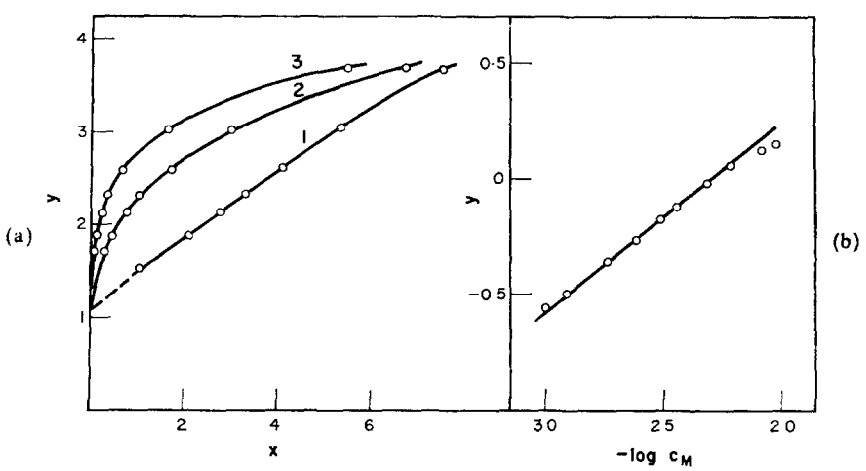

FIG. 5.—Analysis of the $A = f(C_M)$ curve at pH = 2·10, $C_R = 1{\cdot}22 \times 10^{-4}M$, $\lambda = 520$ mμ.

(a) According to equation (5); $y = C_R \times 10^4/(A - A_{0R})$; $x = 1/(C_M{}^m)$ (approximated curves); *1*—$m = 1$; *2*—$m = 2$; *3*—$m = 3$.

(b) According to equation (6); $y = \log \dfrac{A(1 + K_{A1}/[H]) - A_{0R}}{A_{01} - A}$.

Solutions with excess of ligand

The formation of two optically different uranyl(VI) chelates, one at pH < 4 and the other at pH > 6 is clearly shown from the pH–absorbance curves for aqueous equimolar solutions and solution with ligand excess (Fig. 6).

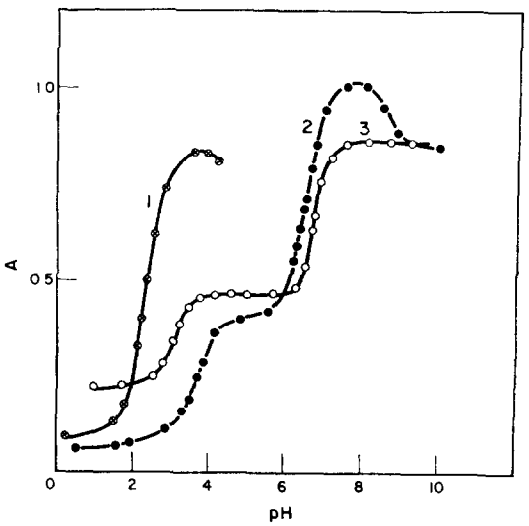

FIG. 6.—pH-Absorbance plots for UO_2-solutions with various concentrations of PAR, at 520 mμ.
1—$C_R = 5{\cdot}15 \times 10^{-5}M$, $C_M = 5{\cdot}15 \times 10^{-3}M$; *2*—$C_R = C_M = 3{\cdot}38 \times 10^{-5}M$; *3*—$C_R = 1{\cdot}35 \times 10^{-4}M$; $C_M = 1{\cdot}35 \times 10^{-5}M$.

Between pH 4 and 6·5 formation of a solid species or of colloidal solutions gives rise to erratic results, but the trouble is avoided by working with 30% v/v dimethylformamide.

The absorbance of the solutions containing excess of reagent was always corrected for absorbance of the surplus reagent at 500–530 mμ, the amount consumed in chelation being taken into account.

The pH–absorbance curve at pH < 3 (Fig. 7) shows the formation of UO_2RH^+, according to equilibria (A) and (B). This chelate coexists with a further chelate which is formed quantitatively at pH $> 7{\cdot}8$–8.

For solutions with excess of ligand the basic equations and transformations follow:

$$C_R \sim [H_2R] + [H_3R^+]$$
$$C_M = [M] + [MRH]$$
$$\Delta A = \varepsilon_{1H}[MRH].$$

When equilibrium (A) is valid,

$$C_M/\Delta A = \frac{1}{\varepsilon_{1H}} + \frac{[H]^2\Delta A(1 + 1/K_{a1}[H])}{[H_3R]k_{12}\varepsilon_{1H}}. \tag{7}$$

When equilibrium (B) is valid,

$$C_M/\Delta A = \frac{1}{\varepsilon_{1H}} + \frac{[H]\Delta A(1 + K_{a1}[H])}{[H_2R]k_{11}\varepsilon_{1H}}. \tag{8}$$

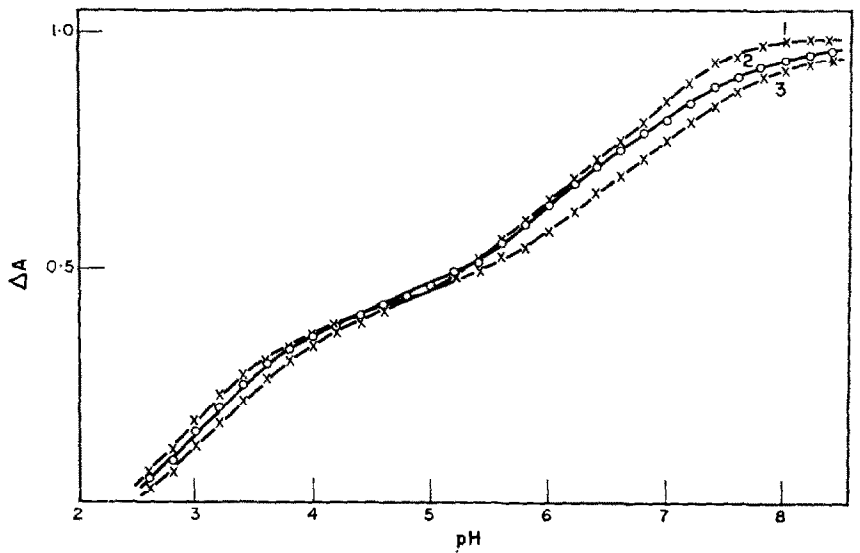

FIG. 7.—pH-Absorbance plots for UO_2^{2+} solutions with various excesses of PAR in the presence of 30% v/v dimethylformamide.
510 mμ; $C_M = 2{\cdot}5 \times 10^{-5}M$; C_R/C_M: *1*—6·37; *2*—12·75; *3*—19·12. The absorbance of the ligand is subtracted.

We also have

$$\log\left\{\frac{\Delta A}{A_{01} - \Delta A}\right\} = \log\{[H]^2(1 + 1/K_{a1}[H])\} + \log[H_3R] + \log k_{12}. \qquad (9)$$

In the second formation region at pH > 6 the principal equilibria must be selected from the following:

$$MRH + H_2R \rightleftharpoons M(RH)_2 + H^+ \qquad (C)$$

$$MR + HR^- \rightleftharpoons MR_2 + H^+ \qquad (D)$$

$$MRH \rightleftharpoons MR + H^+ \qquad (E)$$

$$MRH + HR^- \rightleftharpoons MR_2 + 2H^+ \qquad (F)$$

$$2MRH \rightleftharpoons MR_2 + M^{2+} + 2H^+. \qquad (G)$$

It is difficult to distinguish the equilibria involving ligand from those such as (E) and (G) in solutions with excess of ligand. However, the parts of the pH curves at pH 5·5–7 are slightly shifted to higher pH values with increasing ligand concentration. Further, only 1:1-chelates were found at pH < 8·5 by Job's method and the tangent ratio plots (*vide infra*). Hence no further ligand is co-ordinated to the UO_2RH^+ chelate at pH > 6 and only the equilibria (E) and (G) need to be considered.

The splitting off of one proton according to equations (10), (11) and (12) and the equilibrium (E) was proved by the constant values of the molar absorptivities and the equilibrium constant, K_{Ra1}, obtained when these equations were used for results from solutions with $C_M = 2{\cdot}5 \times 10^{-5}M$, $C_R/C_M = 6$–19 in 30% v/v dimethylformamide, or with $C_M = 2{\cdot}5 \times 10^{-5}M$, $C_R = 2{\cdot}00 \times 10^{-4}M$ in aqueous solutions and over the

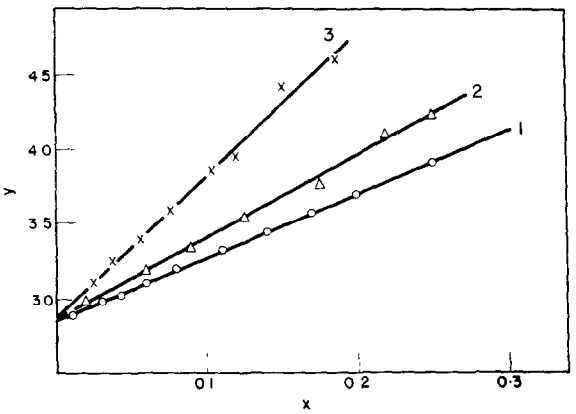

FIG. 8.—Analysis of the second linear portions of the pH-absorbance plots in Fig. 7, according to equation (11).

$y = C_M \times 10^5/\Delta A$; $x = \frac{(\Delta A - \varepsilon_{1H}C_M)[H]}{\Delta A}$; C_R/C_M: *1*—6·37; *2*—12·75; *3*—19·12.

wavelength range 510–520 mμ (Figs. 8 and 9).

$$C_M = [MRH] + [MR]$$

$$A = \varepsilon_{1H}[MRH] + \varepsilon_1[MR]$$

$$K_{kal} = [MR][H]/[MRH]$$

$$C_M/\Delta A = \frac{1}{\varepsilon_{1H}} - \frac{(\varepsilon_1 C_M - \Delta A)K_{kal}}{[H]\Delta A\varepsilon_{1H}} \tag{10}$$

$$C_M/\Delta A = \frac{1}{\varepsilon_{1H}} + \frac{(\Delta A - \varepsilon_{1H}C_M)[H]}{\varepsilon_1 \Delta A K_{kal}} \tag{11}$$

$$\log \frac{\Delta A - \varepsilon_{1H}C_M}{\varepsilon_1 C_M - \Delta A} = pH + \log K_{kal} \tag{12}$$

where ε_1 is the molar absorptivity of the UO_2-PAR complex. The value of ε_{1H} calculated from the intercept of (10), using for ε_1 the value obtained from the horizontal line of the pH curve, agreed well with the value found for solutions with metal ion excess when equation (1) was used. Similarly the same value of ε_1 was obtained from equation (11) when the value of ε_{1H} calculated from equation (1) for solutions with metal ion excess was used. Values of ε_1 and K_{kal} were also calculated for various points of the pH-curve between pH 5·8–7 when this value of ε_{1H} was used in equations (13) and (14):

$$\varepsilon_1 = \frac{a_1\Delta A_2 - a_2\Delta A_1}{C_M(a_1 - a_2)} \tag{13}$$

where $a = (A - \varepsilon_1 C_M)[H]$,

$$K_{kal} = \frac{(A - \varepsilon_{1H}C_M)[H]}{\varepsilon_1 C_M - \Delta A}. \tag{14}$$

The values for ε_1 and K_{kal} agreed well with those found from equations (10), (11) and (12). This agreement is proof that equilibrium (E) predominates.

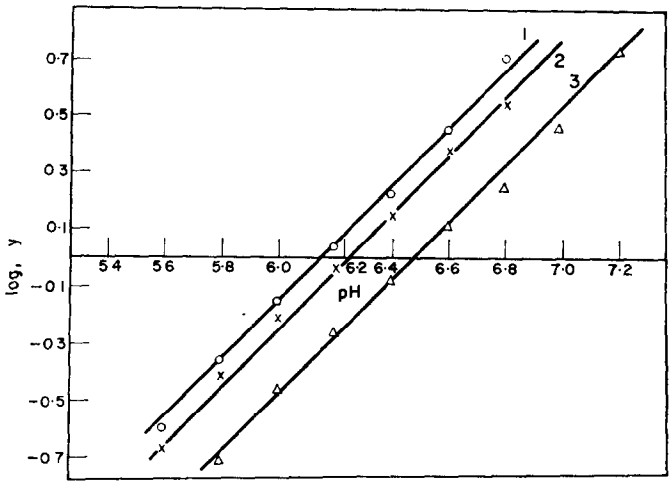

FIG. 9.—Logarithmic plots according to equation (12) for the second linear portions of the pH-absorbance curves in Fig. 7.

$$y = \frac{\Delta A - \varepsilon_{1H} C_M}{\varepsilon_1 C_M - \Delta A}\ ;\quad C_R/C_M\text{: } 1\text{—}6{\cdot}37;\ 2\text{—}12{\cdot}75;\ 3\text{—}19{\cdot}12.$$

No explanation is given for the shift of the linear logarithmic plots (12) to higher pH values with increasing ligand concentration. It seems that the formation of the MRH-complex is preferred and the transition (E) delayed when the concentration of the ligand is increased.

Note: For calculations the absorbance of the total concentration of reagent $C_R = [H_2R] + [HR^-]$ was always subtracted from the measured absorbance, the concentration of ligand bound in chelates being neglected.

Other evidence for the 1:1 *complex*

Continuous variation and slope-ratio plots (Figs. 10 and 11) indicated the existence of a 1:1 complex over the pH range 3·1–8.

Molar absorptivities and constants of the UO_2-chelates

The results calculated by various methods are summarized in Tables II and III for both chelates. The following additional constants were defined to characterize both uranyl-chelates:

$$k_{12} = [MRH][H]^2/[M][H_3R] = k_{11}K_{a1}$$
$$K_{1H} = [MRH]/[M][HR^*] = k_{12}/K_{a2}{}^*K_{a1} = k_{11}/K_{a2}{}^* = k_{11}/K_{a3}$$
$$K_{kal} = [MR][H]/[MRH]$$
$$K_1 = [MR]/[M][R] = K_{kal}K_{1H}/K_{a3}{}^* = K_{kal}K_{1H}/K_{a2}.$$

For an explanation of the equivalence of $K_{a2}{}^*$ with K_{a3}, and of $K_{a3}{}^*$ with K_{a2} see Sommer and Ivanov.[4]

The protonated UO_2RH^+ is a little bit more stable than the normal UO_2R. Of the values of constants given by Geary *et al.*[11] only that of $\log K_1 = 12{\cdot}5$ agrees with $\log K_{1H}$ found here. Since no 1:2-complex with uranium(VI) exists, the values given for $\log K_2 = 8{\cdot}4$ for water or 9·6 for 50% v/v water-dioxane are rather confusing and differ seriously from the value of $\log K_{kal} = 6{\cdot}3$ found in this study.

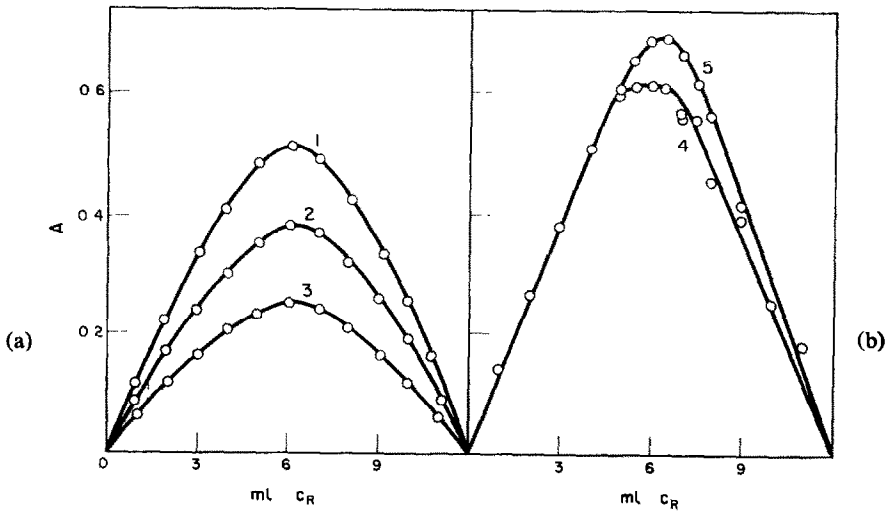

FIG. 10.—Job curves of equimolar solutions of PAR and UO_2^{2+}.
(a) $C_0 = 1{\cdot}375 \times 10^{-4}M$, $\lambda = 520$ mμ: *1*—pH 3·50; *2*—pH 3·25; *3*—pH 3·10.
(b) $C_0 = 9{\cdot}444 \times 10^{-6}M$, $\lambda = 520$ mμ: *4*—pH 8·10 (0·08*M* triethanolamine); *5*—pH 8·01 (0·04*M* triethanolamine).

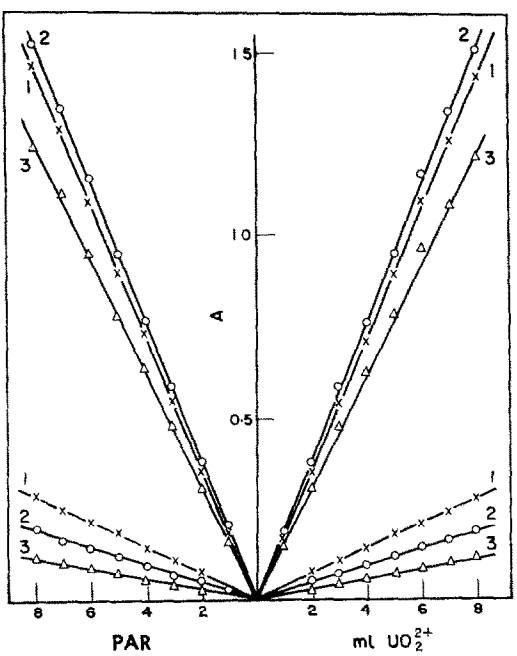

FIG. 11.—Slope-ratio plots.
1—510 mμ; *2*—530 mμ; *3*—550 mμ. Upper lines for pH 7·68 and 0·2*M* triethanolamine, lower lines for pH 4·80 and 0·2*M* acetate. $C_R = 1{\cdot}0 \times 10^{-4}M$, $C_M = 5 \times 10^{-6}$–$4 \times 10^{-5}M$, or *vice versa*.

TABLE II.—MOLAR ABSORPTIVITIES OF URANIUM(VI)-PAR CHELATES

	$UO_2(PAR)H^+$				$UO_2(PAR)$		
Wavelength, $m\mu$	500	510	520	530	510	530	
$\varepsilon \times 10^{-4}$	1·87*	1·93† 1·81*	1·68*	0·85‡	3·51¶ 3·48**	3·76¶ 3·81†† 3·76‡‡ 3·90¶¶ 3·95***	3·87¶¶

* Equation (1), $C_R = 5{\cdot}15 \times 10^{-5}M$, $C_M/C_R = 100$.
† Equation (1), $C_M/C_R = 20$–100 (mean of 5 values).
‡ At pH 3·6 in presence of 0·1M formate.
¶ Equation (13).
** Equation (11), $C_R/C_M = 6{\cdot}4$–$19{\cdot}1$ (mean of 4 values).
†† $C_R/C_M = 10$, pH 7·68 (0·1M triethanolamine), mean of 8 values.
‡‡ From $\Delta A = \varepsilon_1 C_M$, at pH 8·05 (0·1$M$ tris(hydroxymethyl)aminomethane), mean of 8 values.
¶¶ *Cf.* Florence and Farrar.[3]
*** At pH 8 (0·1M triethanolamine).

Note: For ε_1 according to equations (11) and (13) the values for 510 mμ were recalculated from those for 530 mμ by using the average ratio, $A_{530}/A_{510} = 1{\cdot}07$, evaluated from absorption curves for solutions with a 6 to 19-fold excess of ligand at various pH values.

TABLE III.—VALUES OF EQUILIBRIUM CONSTANTS OF URANIUM(VI)-PAR CHELATES

$\log k_{12}$*	$\log k_{11}$	$\log K^*_{kal}$	$\log K_{1H}$*	$\log K_1$
−2·12 (3)	0·98	−6·29 (14)†	12·9	11·9
−2·3 (3)		−6·41 (12)†	12·7 (3)	
−2·3†		−6·61‡		

The equation used is identified by the number in brackets.
* Average of at least 3 values.
† In 30 v/v dimethylformamide.
‡ In solutions with $C_R = C_M$ and $C_R/C_M = 10$.

The nature of the solid products

To a 1M perchloric acid solution containing 100 μg of uranyl ion and 50 ml of $1{\cdot}25 \times 10^{-2}M$ PAR, 0·5M ammonia was added dropwise (the ratio UO_2:PAR was 5:7). The solution was carefully shaken and left for some hours in a dark place. Two slightly different crystalline solids were precipitated at pH 1·84 and pH 3·35. They were filtered off on sintered glass, washed with a little ethanol and water and then dried over silica gel in a vacuum desiccator. The hues of the dry solids are quite different—deep red and dark brown-red. The solids were analysed (found for precipitate obtained at pH 1·84: C 35·0%; H 3·0%; N 10·3%; U 24·9%; H_2O 7·1%, and for precipitate obtained at pH 3·35: C, 30·8%; H 3·5%; N 9·7%; U 36·1%); the elemental ratios found were U:N = 1:7 and 1:4·6, U:C = 1·28 and 1:17, respectively. The compounds are evidently of variable or non-stoichiometric composition, but that there is more than one ligand molecule per uranium atom in the solid state seems to be proved. The amount of ligand in the solid species possibly decreases as the pH of precipitation is raised.

Comments on the spectrophotometric determination of uranium with PAR

The methods due to Geary *et al.*,[1] Busev and Ivanov,[2] and Florence and Farrar[3] at pH 8 result in the quantitative formation of UO_2(PAR), which has a high molar absorptivity. The very useful mixture of 1,2-diaminocyclohexanetetra-acetic acid, fluoride and 5-sulphosalicylic acid for masking interfering ions increases the selectivity of the reaction at pH 8. The working conditions and triethanolamine buffer recommended by Florence and Farrar[3] can be fully endorsed.

Sometimes the presence of 0·1–0·2*M* triethanolamine alone guarantees good buffering capacity at pH 8 and partial masking of a number of univalent ions. The minimal ligand excess during the work should correspond to $C_R/C_M = 8$. The absorbance is fairly independent of the order of mixing the components and of the ionic strength of the solution and is little influenced by the buffer up to 0·2*M* concentration. The Lambert-Beer law is obeyed up to 7·5 ppm of uranium(VI) and the spectrophotometric sensitivity is 0·006 $\mu g/cm^2$ for $A = 0{\cdot}01$ at 530 mμ.

Determination at pH 3·6

In this case the quantitative formation of protonated UO_2(PAR)H^+ forms the basis of the method. In the presence of $\geqslant 20\%$ v/v dimethylformamide or of formate as buffer no precipitation occurs and the Lambert-Beer law is obeyed up to 12·3 ppm of uranium(VI). Increasing concentration of formate decreases the absorbance of the solution at 530 mμ (Fig. 12); hence its concentration must be the same for the sample and standards. A minimal reagent ratio of $C_R/C_M = 8$–10 and a formate

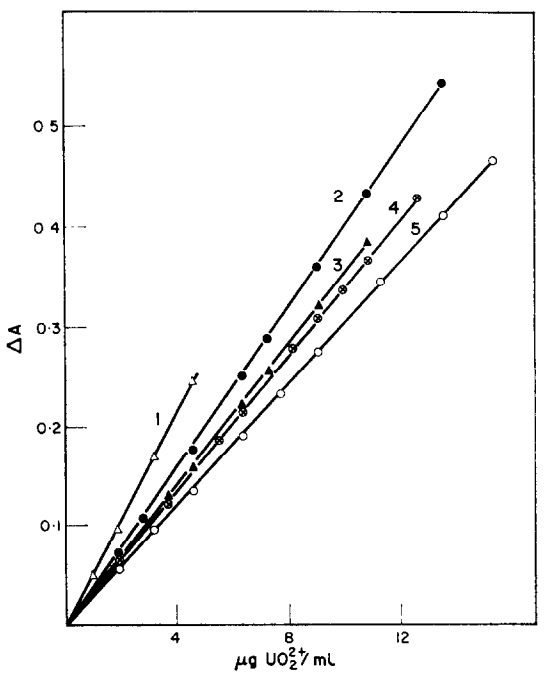

FIG. 12.—Calibration curves at pH 3·60.
$C_R = 3{\cdot}24 \times 10^{-4}M$, $\lambda = 530$ mμ. *1*—without buffer; *2*—20% v/v dimethylformamide; *3*—0·06*M* formate; *4*—0·08*M* formate; *5*—0·1*M* formate.

TABLE IV.—INTERFERENCES OF SOME SUBSTANCES IN THE DETERMINATION OF URANIUM(VI)

Substance	pH 3·6*		pH 8·0†	
	Taken, *ppm*	Error, %	Taken, *ppm*	Error, %
Bicarbonate	1186	−5·0	30·5	−5·0
Acetate	163	+4·0	8·2	+5·0
Tartrate	35	−5·4	3510	−5·5
Oxalate	1	−6·6	138	−5·0
EDTA	114	−5·0	59·5	−5·8
Th(IV)	3	+5·0	3	+4·9
Y(III)	19	+5·0	0·05	+5·0
La(III), Ce(III), Pr(III), Nd(III)	75–80	+5·0	0·1–0·05	+5·0

* 7·75 ppm uranium, $C_R = 1{\cdot}935 \times 10^{-4}M$, 0·1*M* formate.
† 2·9 ppm uranium, $C_R = 9{\cdot}68 \times 10^{-5}M$, 0·1*M* triethanolamine.

concentration of not more than 0·1 *M* are recommended. Inert salts do not influence the absorbance even in high concentrations. The spectrophotometric sensitivity is 0·027 μg/cm^2 for $A = 0{\cdot}01$ at 530 mμ in the presence of 0·1*M* formate buffer. The sensitivity is only a quarter of that at pH 8 but the higher selectivity is advantageous. The interference of rare earths and a number of anions decreases. The influence of some interfering substances is summarized in Table IV. Beryllium does not interfere at pH 3·6 even in large amounts.

Zusammenfassung—Das Uranylion bildet mit 4-(2-Pyridylazo)resorcin (PAR) nur 1:1-Chelate in Lösungen mit pH <8,5, und zwar UO_2-(PAR)H$^+$ bei pH >3 und UO_2(PAR) bei pH >5,5. Es werden Gleichgewichtskonstanten und spektrophotometrische Daten für beide Chelate angegeben. Feste, nichtstöchiometrische kristalline Spezies, in welchen das Molverhältnis von PAR zu Uran höher als 1:1 ist, werden bis pH 6 gefällt. 0,1–0,2 M Triäthanolamin, das von anderen Autoren bei pH 8 empfohlen wird, erwies sich als zufriedenstellend für die empfindliche spektrophotometrische Bestimmung von Uran, ferner bei pH, 3,6 in Gegenwart von ≤0,1 M Formiat oder 20–30 Volum-% Dimethylformamid.

Résumé—L'ion uranyle et le 4-(2-pyridylazo) résorcinol (PAR) ne forment que des chélates 1:1 en solutions de pH < 8,5 UO_2(PAR)H$^+$ se formant à pH > 3 et UO_2(PAR) à pH > 5,5. On fournit les constantes d'équilibre et les données spectrophotométriques pour les deux chélates. Des espèces cristallines solides, non stoechiométriques, dans lesquelles le rapport molaire PAR-uranium est plus que 1:1 sont précipitées jusqu'à pH 6. Le milieu triéthanolamine 0,1–0,2*M* à pH 8 recommandé par d'autres auteurs s'est révélé satisfaisant pour le dosage spectrophotométrique sensible de l'uranium, ainsi que le milieu pH 3,6 en présence de formiate <0,1*M* ou de diméthylformamide 20–30% v/v.

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DETERMINATION OF TERTIARY AMINES AND SALTS OF ORGANIC ACIDS IN ACETIC ACID BY CATALYTIC THERMOMETRIC TITRATION

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Summary—A new method of determination of tertiary amines and salts of organic acids in acetic acid solution, to which about 2% of water and 8% acetic anhydride are added, is described. After the equivalence point, the excess of perchloric acid catalyses the exothermic reaction of water with acetic anhydride. The end-point is determined from the graph of temperature against volume of added titrant. If a slightly soluble compound is produced during the titration, the precision of the new method is superior to that of the potentiometric method.

IT is known that by the hydrolysis of acetic anhydride a considerable amount of heat is liberated, but that the process is slow. However, strong acids accelerate this hydrolysis.[1] This reaction was successfully applied by Greathouse *et al.*[2] for the determination of acetic anhydride and water in glacial acetic acid by thermometric titration. Keily and Hume[3] determined by thermometric titration different weak organic bases and salts of organic and inorganic acids by titrating them with perchloric acid in glacial acetic acid. The titration system should not contain at the same time water and acetic anhydride, since these two components, though reacting only slowly before the equivalence point, start a violent reaction after reaching that point in the presence of a slight excess of perchloric acid as catalyst. A sudden and uncontrolled increase in temperature after the equivalence point makes thermometric titration of bases impossible, even if the differential method is applied. Temperature changes at the titration end-point are slight (less than 0·1°), and the titration curve is of the usual shape, *i.e.*, it rises linearly to the equivalence point, and then it drops, also linearly.

As has been seen, the reaction between water and acetic anhydride is a disadvantage for thermometric titrations in glacial acetic acid. On the basis of this reaction we have, however, been able to develop a new procedure based on the following principles: the base is titrated in glacial acetic acid containing a certain amount of water and acetic anhydride, with a perchloric acid solution in glacial acetic acid. The reaction between water and acetic anhydride is slow till the equivalence point, but after it, with the first excess of perchloric acid, it shows a sudden acceleration. A particular problem was the determination of the titration end-point, and we developed three methods for determining it: from the intersection of two straight lines, from the intersection of a straight line and a curve, or by means of a calibration curve.

The method is based on the titration of bases with perchloric acid, which acts as a catalyst in the water-acetic anhydride, and it should, therefore, be classified as a

"catalymetric" titration.[4] Because the titration end-point is determined from the increase in temperature, as in thermometric titrations, we propose the name catalytic-thermometric titration for this type of analysis. On a similar principle Vaughan and Swithenbank[5] determined weak acids in acetone, by titrating them with a 1*M* solution of potassium hydroxide in isopropanol. At the end-point, the free potassium hydroxide caused polymerization of the acetone, giving a large temperature rise.

EXPERIMENTAL

As solvent we used glacial acetic acid (C. Erba, s.g. 1·051 and Oswiecim zaklady chemiczni, s.g. 1·049–1·060) mixed with acetic anhydride (C. Erba, s.g. 1·08), in the ratio 12:1. The 0·25*M* solution of perchloric acid (Kemika *p.a.*, s.g. 1·07) in glacial acetic acid was standardized potentiometrically with sodium acetate, a Radiometer pH meter type pH M 22 m being used. For potentiometric determination of the substances used, as well as for the standardization of perchloric acid, a glass electrode was used coupled with a mercury/mercury(I) acetate electrode.[6] When halogen acid salts of organic bases were titrated, a 3% mercuric acetate solution was added. Because of the expansion of the glacial acetic acid as the temperature rose during titration, the necessary corrections to the molarity of the titrant were always made.[7] Titrations were made by means of a calibrated Metrohm piston burette, type E 274, 20-ml capacity, scale graduated to 0·02 ml. Temperature was measured with either a thermometer or a thermistor.

For thermometric operations the 50-ml beakers used were lined on the outside with tinfoil and placed in 100-ml beakers, and these were then placed in 400-ml beakers which were lined on the inside with filter paper and had a perforated cork insulator at the bottom. The solutions were stirred magnetically. Experiments were also carried out in Dewar vessels, though the results obtained when using ordinary glass beakers were satisfactory.

RESULTS AND DISCUSSION

The solvent selected contained 8% of acetic anhydride and 2% of water. The mechanism of the exothermic reaction between water and acetic anhydride is not yet definitely known.[8] We measured the reaction rate as a function of the quantity of perchloric acid added as catalyst at the initial temperatures of 22° and 28°, by following temperature changes in the reaction mixture (total volume 26 ml). The results obtained at 28° are shown in Fig. 1. The graph obtained at 22° is of similar shape, but the reaction rate is lower.

If, on the basis of the values from Fig. 1, a graph is plotted of temperature rise against the amount of perchloric acid present, the function is linear if temperature readings are taken less than 2 min after each addition of reagent, independent of the initial temperature of the solution. Therefore, if the addition of perchloric acid is made at equal intervals of time, the increase in temperature must be exponential in character, even if the exponential effect of temperature on the reaction rate is left out of account. This is evident if the temperature changes during titration are plotted either on ordinary or semi-log paper (Figs. 2a and 2b). When plotted on ordinary paper, the temperature curve rises linearly to the equivalence point, and then exponentially if the readings are taken at 1-min intervals after addition of the titrant. If, however, the temperature changes are plotted logarithmically, the values before the equivalence point lie on a curve, and on a straight line after it. The equivalence point is easily determined from the intersection of the lines.

To determine the end-point from a graph plotted on ordinary paper, we developed the following procedure. The titration is carried out by adding equal amounts of titrant at equal intervals of time to the solution titrated, and reading the temperature at a given time after adding the titrant, *e.g.*, 1 min. The equivalence point is reached when there is a sudden temperature rise. Then yet another point is determined in the same manner, while the subsequent reading is taken at half the time interval. Thus

three more points are obtained after the equivalence point. By connecting the points two straight lines are obtained, the intersection of which is the titration end-point (Fig. 2a). The figures circled represent the values after which no more titrant is added. Temperature readings can also be started when 75% of the base has been titrated. To determine the end-point precisely from the graph on ordinary paper, it is imperative to know the maximum temperature rise caused by 0.10 ml of 0.25*M* perchloric acid at the working temperature. These maximum temperature changes for a total volume

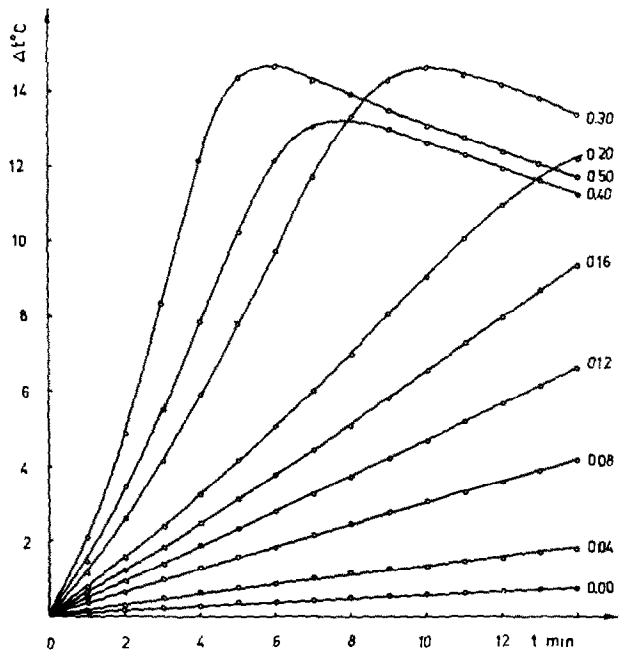
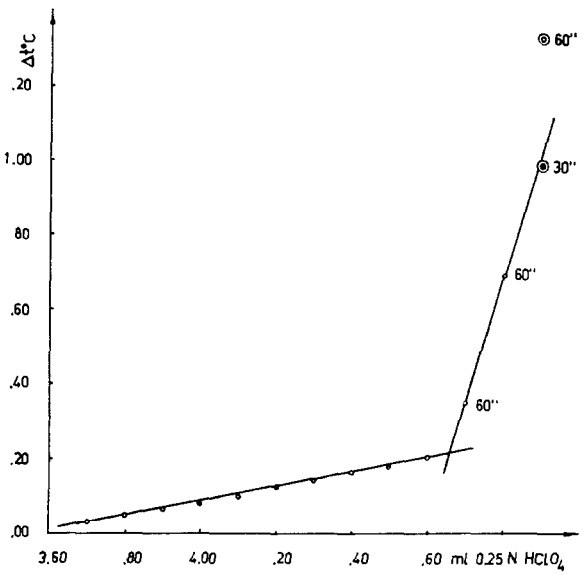


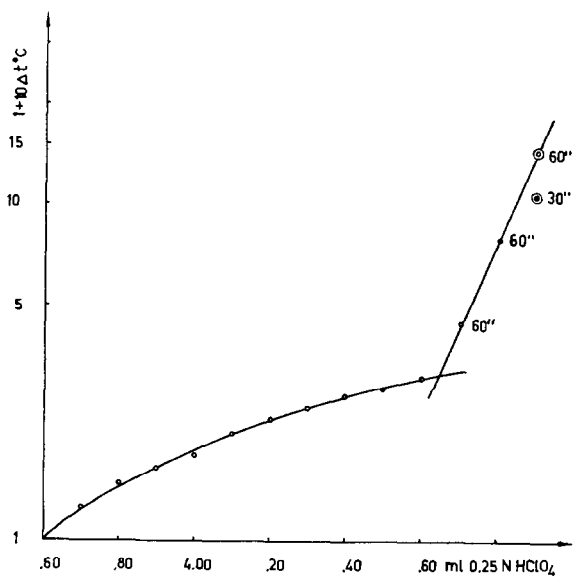
FIG. 1.—Changes in rate of reaction of water and acetic anhydride with change in concentration of perchloric acid, at 28°C.

of 26 ml at different initial temperatures are shown in Fig. 3. The end-point can be determined without this function being known, but if the temperature rise after the end-point is too large or too small, this function can be used to resolve the dilemma of whether the temperature measured is to be taken as the first or the second point used to obtain the straight line after the equivalence point.

The end-point can also be determined by means of a calibration curve based on the data given in Fig. 1. The product of the temperature change and the total volume of solution is plotted against the volume of perchloric acid added. Straight lines are obtained, the slopes of which depend on the initial temperature and the time at which the temperature readings are taken. The titration is continued until the first increase in temperature after the equivalence point. Temperature readings are taken every minute, but no more perchoric acid is added to the solution. The effect of the catalyst in the water–perchloric acid–acetic anhydride system is proportional to its amount, and so this excess of perchloric acid can be determined from the calibration curve. The results and average deviation obtained by the first two methods (Figs. 2a and 2b)



(a)



(b)

FIG. 2.—Catalytic thermometric titration curves for sodium acetate (a) on ordinary paper, (b) on semi-log paper.

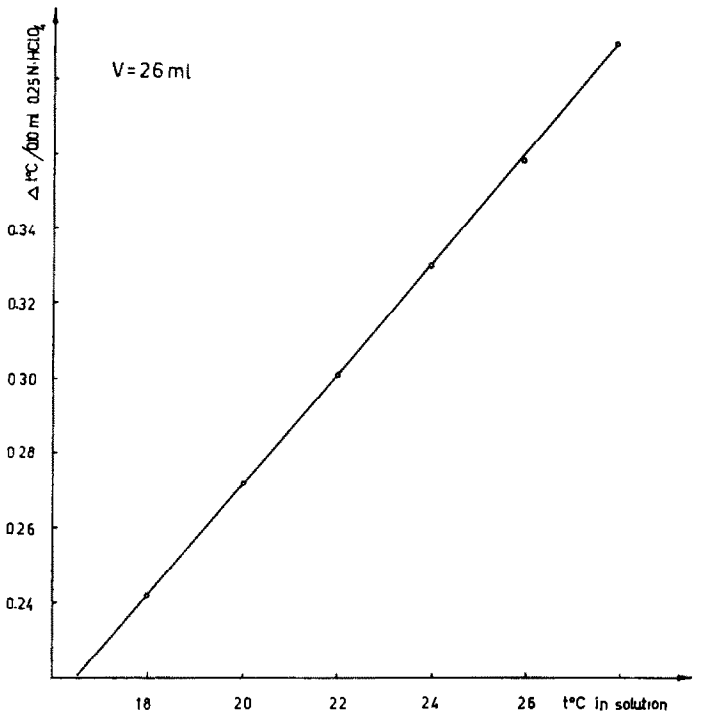


FIG. 3.—Temperature change on addition of 0·10 ml of 0·25*M* perchloric acid to 26 ml of solution, as a function of temperature.

TABLE I.—COMPARISON OF RESULTS OBTAINED BY POTENTIOMETRIC AND CATALYTIC THERMOMETRIC TITRATIONS

Substance titrated	Taken, *g*	Potentiometric titration			Catalytic thermometric titration		
		No. of titrations	Found, *g*	Average deviation %	No. of titrations	Found, *g*	Average deviation %
Aminopyrine	0·1500	4	0·1498	0·35	6	0·1495	0·29
Antipyrine	0·2000	4	0·2000	0·11	8	0·1942	0·11
Cinchonine	0·1000	9	0·0972	0·20	9	0·0970	0·21
Flagyle*	0·2000	4	0·1999	0·79	5	0·1985	0·42
Intra-iodine†	0·2000	4	0·1994	0·39	6	0·1999	0·06
Inversal‡	0·2000	10	0·1850	0·11	10	0·1858	0·08
Potassium biphthalate	0·2000	3	0·2012	0·11	3	0·2016	0·21
Sodium acetate	0·1500	4	0·1500	0·15	6	0·1501	0·23
Sodium benzoate	0·1500	3	0·1498	0·06	6	0·1496	0·03
Sodium formate	0·1000	3	0·0996	0·38	6	0·0990	0·17
Sodium salicylate	0·2000	3	0·2008	0·30	6	0·2007	0·11
Triethylamine	0·1500	3	0·1500	0·03	6	0·1503	0·07
Pyridoxine-HCl§	0·2000	8	0·2021	0·19	9	0·2016	0·21

* *β*-Oxyethyl-2-methyl-5-nitro-imidazole
† 1,3-Triethylammonium-2-propanol iodide
‡ *p*-Benzoquinoneamidinohydrazonethiosemicarbazone
§ 5-Hydroxy-6-methyl-3,4-pyridinedimethanol hydrochloride

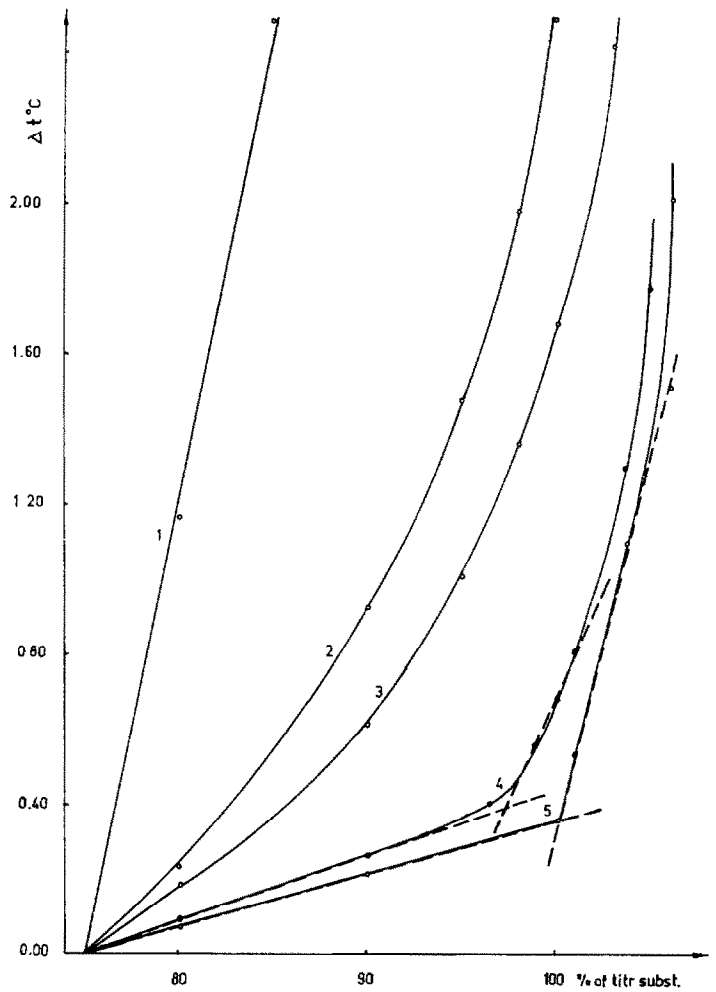


FIG. 4.—Catalytic thermometric titration curves for bases of different strengths: *1* — caffeine; *2* — 2-methyl-5-nitro-imidazole; *3* —novalgin; *4* —antipyrine; *5* — potassium biphthalate.

are in good agreement with those achieved potentiometrically, but in the calibration curve method the deviations are considerable.[9]

By the catalytic thermometric method described, the determinations of bases are improved as the potential change around the equivalence point increases. Very weak bases, such as caffeine or 2-methyl-5-nitro-imidazole, cannot be determined under these conditions, since their basicity is already so weak that the catalytic reaction takes place in preference to neutralization. Titration curves for such bases, plotted on ordinary paper, are given in Fig. 4. As can be seen, antipyrine cannot be determined precisely (the error amounts to −2·8%), whereas with potassium biphthalate a pronounced rise in temperature appears immediately after the disappearance of the base from the solution, *i.e.*, the end-point is identical with the equivalence point. The results of determinations by this method are much more reproducible than those

obtained potentiometrically, if the substances titrated give precipitates with perchloric acid. This can be seen from Table I, where results and average deviations are given for determinations by both methods. The concentrations of the bases ranged from $2{\cdot}5 \times 10^{-2}$ to $5{\cdot}7 \times 10^{-2}N$, and the quantities taken were from 0·63 to 1·4 mequiv. Even lower concentrations can be titrated by this method.[9]

In comparison to the results obtained by various electrochemical methods developed earlier and described in previous papers, [10–13] it can be seen that the new method gives high accuracy and reproducibility.

Acknowledgement—We express our gratitude to the Pharmaceutical Industry "Galenika", Beograd for supplying us with the samples of the substances investigated.

Zusammenfassung—Es wird eine neue Methode beschrieben, tertiäre Amine und Salze organischer Säuren in Essigsäurelösung, welcher etwa 2% Wasser und 8% Acetanhydrid zugefügt werden, zu bestimmen Nach Erreichen des Äquivalenzpunktes katalysiert die überschüssige Perchlorsäure die exotherme Reaktion von Wasser mit Acetanhydrid. Der Endpunkt wird durch die graphische Darstellung der Temperatur gegen das Volumen des zugefügten Titranten bestimmt. Falls sich während der Titration eine schwerlösliche Verbindung bildet, ist die Genauigkeit der neuen Methode der potentiometrischen überlegen.

Résumé—On décrit une nouvelle méthode de dosage des amines tertiaires et des sels d'acides organiques en solution dans l'acide acétique auquel on ajoute environ 2% d'eau et 8% d'anhydride acétique. Au-delà du point d'équivalence, l'excès d'acide perchlorique catalyse la réaction exothermique de l'eau avec l'anhydride acétique. Le point de fin de dosage est déterminé à partir de la courbe de la température en fonction de volume d'agent de titrage ajouté. Si, lors du dosage, il se forme un composé faiblement soluble, la précision de la nouvelle méthode est supérieure à la méthode potentiométrique.

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HYDROXYTRIAZENES—A REVIEW OF A NEW CLASS OF CHELATING AGENTS

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Summary—A review of the applications of hydroxytriazenes as chelating agents in analytical chemistry.

THE new class of organic reagents, hydroxytriazenes, is of comparatively recent origin. This review gives a survey of analytical applications of this potentially useful class of organic reagents.

Since the syntheses of hydroxytriazenes by Bamberger[1] and others,[2] the complexing ability of these compounds has been examined by Elkins and Hunter.[3] They reported that these compounds form well defined crystalline complexes with Cu(II), Ni(II), Co(II), Co(III), Fe(II) and Fe(III), but Sogani and Bhattacharya[4] first evaluated their analytical usefulness. Sogani and co-workers later prepared a large number of these compounds and discussed and described their analytical use.[5–8]

Two methods have been reported for the preparation of these compounds:

(i) by the action of phenylhydrazine or substituted phenylhydrazine[1] on aliphatic or aromatic nitro or nitroso compounds

(ii) by the coupling reaction of diazo compounds[4] with alkyl or aryl-substituted hydroxylamines.

The latter method seems to have been preferred. These compounds possess the common functional grouping —N(OH)—N=N—.

Ultraviolet and infrared absorption studies of a large number of hydroxytriazenes have been made and an intramolecular hydrogen-bonded structure has been assigned.[9] In the case of 3-hydroxy-1,3-diphenyl triazene, an intramolecular hydrogen-bonded structure and its tautomeric forms have been postulated[10] on the basis of its acid dissociation constant and ultraviolet absorption. Tautomerism is also reflected in the synthesis of both the *O*- and *N*- ethers.[11]

3-*Hydroxyl*-1,3-*diphenyltriazene*

This is a light yellow compound, m.p. 119–120°. Its spectral characteristics in alcohol are: λ_{max} 238 and 348 mμ; log ε 4·186 and 4·328 respectively. It is stable towards heat, light, and air, and can be preserved indefinitely. Many of its complexes are granular, insoluble in water, thermally stable, of definite composition, and suitable for direct weighing. The reagent is not very soluble in water but the excess of the reagent can be removed easily either by washing with dilute alcohol or by

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heating the weakly acidic solution to hydrolyse it to water soluble products. The washings can be checked for presence of reagent by addition of a drop of sodium hydroxide solution. If alcohol has been used an intense yellow colour appears, and a blue colour if the reagent was hydrolysed. Below pH 3 the reagent precipitates only Cu(II), Pd(II), Fe(III), V(IV), Ti(IV), and molybdate. Only the first two are stable if the acidic reaction medium is heated.

Estimation of palladium. A granular yellowish green palladium(II) complex is quantitatively precipitated between pH 1·6 and 8. It is soluble in acetone, chloroform, carbon tetrachloride and benzene, and crystallizes from acetone as silky yellowish brown needles, m.p. 252°. Spectral characteristics in alcohol are λ_{max} 255 and 413 mμ with log ε 4·585 and 4·384 respectively.

In estimations the pH is kept between 2 and 3 (hydrochloric acid and sodium acetate) and a 20–25% excess of the reagent is added. Palladium can be estimated in the presence of Ni, Co(II), Zn, Al, Cr(III), Cd, Mn(II), Sb(III), Bi(III), As(III) Be, UO_2(II), Fe(III), Zr, Ce(IV), and nitrate. In separations from Ce(IV) and Zr(IV), no sodium acetate or sodium potassium tartrate should be added, the pH being adjusted by dilution only, as prolonged heating in the presence of buffering agents causes a turbidity and high results. Au(III), Ag(I), and Os(IV), interfere by being reduced to the metallic state by the reagent. Pt(IV) even in 10-fold times excess does not interfere. Separation from Rh(IV), Ru(III), Ir(III), Th, Sn(IV), Pb, Ti, molybdate, fluoride, and phosphate has also been described. No actual separation of palladium from alkali or alkaline earth metals has been carried out but none of these elements forms a precipitate with the reagent, so they should be separable. The reagent is said to be superior to dimethylglyoxime.

Estimation of copper. A granular chocolate brown copper complex is completely precipitated between pH 1·9 and 7 with a slight excess of the reagent. The complex is highly soluble in benzene, chloroform, and carbon tetrachloride, fairly soluble in ether and acetone, and only slightly soluble in alcohol. It crystallizes from acetone as brown silky needles, m.p. 193°. Spectral characteristics in alcohol are: λ_{max} at 247, 283 and 362 mμ, log ε 4·563, 4·132, and 4·572 respectively.

Estimations are carried out between pH 2·3 and 3·0 to facilitate hydrolysis of excess of reagent and increase specificity. Cu(II) (13–17 mg) has been determined in the presence of 50 mg of Ni, Zn, Mn(II), Cd, Bi(III), Al, Cr(III), Hg(II), As(III), Pb, Sb(III), Zr, UO_2(II), Ce(IV), Th, Be, Co(II), Fe(II), Fe(III), Ti, Sn(IV), nitrate phosphate, fluoride, tungstate, and molybdate. Ag(I), Au(III), and Os(IV) interfere by reduction to the metallic state by the reagent, but this reaction may be prevented by addition of cyanide. Copper cannot be estimated in the presence of palladium, and cannot be separated quantitatively from V(V), and V(IV), because of their partial coprecipitation.

The reagent has been reported[12] to be superior to all the copper reagents described in the literature, including salicylaldoxime and α-benzoinoxime.

Estimation of nickel. Nickel is precipitated quantitatively between pH 4·4 and 7·0. The deep yellow complex has solubility properties similar to those of the copper complex, and crystallizes from acetone as bright yellow needles, m.p. 209°. Spectral characteristics in alcohol are λ_{max} 248, 320 and 410 mμ and log ε 4·455, 4·391, and 4·199 respectively. Nickel has been estimated between pH 5·0 and 5·5 in the presence of Zn, Mn(II), Cd, Mg, As(III), Be, phosphate and fluoride.

Reaction with titanium. The reagent precipitates titanium quantitatively,[12] but the complex is substantially soluble when the concentration of alcohol in the reaction medium is above 5%. The complex also decomposes if the medium is heated above 55°, and is therefore unsuitable for direct weighing.

Vanadium complex. Dutta and Lahiry[13,14] have made a detailed structural study of V(V) and V(IV) complexes of 3-hydroxy-1,3-diphenyltriazine. With the aid of X-ray powder patterns, IR spectra, molecular weights, and magnetic moments they have given a convincing proof that V(V) and V(IV) form the same complex with the reagent, *i.e.*, first V(V) is reduced to V(IV) by the reagent and then V(IV) forms the complex. Reactions of the complexes with pyridine have also been described. A preparative study of V(IV) and V(V) complexes of a number of hydroxytriazines[15] has been reported and reactions of the complexes with pyridine and picoline were also carried out, but so far no attempt has been made to estimate vanadium in either oxidation state with this reagent.

Copper and cadmium separation. Recently the reagent has been used fori dentification and separation of copper and cadmium by Poonia and Gupta.[16]

Electrochemical reduction and polarographic behaviour of 3-hydroxy-1,3-diphenyltriazine. The reduction process for the reagent is reported to be irreversible, with half-wave potential dependent on concentration, *e.g.*, at pH 2·18, $E_{1/2}$ varies from −0·723 to −0·685 V as concentration varies from 0·3 to 0·1 × $10^{-3}M$. A different reduction mechanism at different pH values has been suggested, but the ultimate reduction products have been reported to be the same, *i.e.*, aniline and phenylhydrazine. A polarographic method has been recommended for the detection and estimation of 3-hydroxy-1,3-diphenyltriazene.[17]

3-*Hydroxy*-1-(p-*chlorophenyl*)-3-*phenyltriazene*

This is a light greenish yellow compound, m.p. 140°. Spectral characteristics in alcoholic solution are λ_{max} 235, 281, and 350 mμ, log ε 3·991, 3·874, and 4·183 respectively.

Estimation of titanium.[12] This reagent precipitates titanium quantitatively as a bright orange complex, which is stable up to 100° in an aqueous acidic reaction medium. The optimum pH was found to be between 2·2 and 2·5. The complex crystallizes from alcohol as bright yellow crystals, m.p. 146°. With this reagent, Ti (10 mg) has been estimated in the presence of 50 mg each of Zn, Mn(II), Cd, Co(II), Ni, Hg(II), As(III), UO_2(II), Th, Mg, Cr(III), and Al. The complex is not, however, of definite composition and has to be ignited to titanium dioxide before weighing. Zr, Ce(IV), Cu(II), Pd(II), Fe(II), Fe(III), Mo(VI) and V(V), interfere because of coprecipitation. Phosphate and tungstate precipitate the corresponding titanium salts and hence interfere in the determination.

The reagent however compares well with other reagents for titanium and is superior to the related compounds, cupferron and *N*-benzoylphenylhydroxylamine.

The reagent offers no advantage over the parent compound of the series for the estimation of palladium, copper, and nickel.

3-*Hydroxy*-1-(o-*nitrophenyl*)-3-*phenyltriazene*[18]

This is an orange red compound, m.p. 150°, reported as a qualitative reagent for detection of nickel and zinc in the presence of Fe(II), Fe(III), Al and Mn(II).

With zinc at pH 5–6 it forms a red precipitate (dilution limit 1 in 3×10^4) and with nickel a violet precipitate (dilution limit 1 in $5{\cdot}2 \times 10^4$). It has been used for the colorimetric determination of zinc in ores.[19]

3-Hydroxy-1-(p-nitrophenyl)-3-phenyltriazene

The compound is greenish yellow, insoluble in water, soluble in alcohol, acetone and toluene and gives a yellow solution. With strong alkali a red colour develops. The reagent has been reported by Pochinok *et al.*[20,21] for the detection and colorimetric determination of magnesium. In alkaline solution the colour changes from yellow to orange to red between pH 11 and 12. A 0·05% solution of the reagent is prepared in alcohol and 2–3 ml of this solution are added to 100 ml of 1% sodium hydroxide solution for further use. With magnesium in neutral or weakly acidic medium it develops a rose-violet or blue-violet colour depending on the concentration of magnesium. The detection limit is 1 ppm. If the magnesium concentration is greater than 0·05 mg/ml, precipitation takes place. Alkali metals, alkaline earths, and lead do not interfere. Cations of the third and fourth analytical groups, which are precipitated by sodium hydroxide, do interfere and should be removed. The most intense colour is with magnesium, stable for 1 hr, is reported to be obtained with a reagent containing 2 g of borax 0·6 g of sodium hydroxide, 100 ml of water and 3 ml of a 0·05% alcoholic solution of the reagent.

3-Hydroxy-1-(p-sulphophenyl, sodium salt)-3-phenyltriazene

This is a light yellow water-soluble compound and forms water-soluble complexes. The solid starts decomposing at 157°, and the acid has a pK value of 9·99. Spectral characteristics are λ_{max} 235 and 345 mμ; log ε 4·178 and 4·441 respectively. It has been used as a colorimetric reagent for various metal ions.

Palladium. Sogani and Bhattacharya[22] were the first to synthesize this compound and to report it as a colorimetric reagent for palladium. A spectrophotometric and conductometric study of the palladium complex has been made by Durgapal and Sogani.[23] The composition of the complex is reported to be PdR_2 (where R is the anion of the reagent). Maximum absorbance is at 413 mμ, but to avoid interference the reagent wavelength of 420 and 430 mμ have been used. The sensitivity of the colour reaction is reported to be 0·05 ppm, and the identification limit as 0·05 μg of palladium in 0·15 ml of solution. The optimum pH range for maximum absorbance is between 1·7 and 4·4, but 2·5–3 is preferred. Colour development is instantaneous and maximum colour development is ensured with a 3-fold excess of reagent. Beer's law is obeyed over the concentration range 0·2–5 ppm. From 25° to 85° there is no change in absorbance. Palladium has been estimated in the presence of Cu(II), Ni, Fe(III), Co(II), Pt(IV), Rh(IV), Ir(III) and Ru(III). The reagent is claimed to be superior to other spectrophotometric reagents for palladium.

Iron. With Fe(III) it forms a bluish black water-soluble complex with absorption peaks at 520 and 650 mμ, in the pH range 2–4·3. The composition FeR_3 has been established by conductometric and spectrophotometric methods.[24] Both methods have indicated that FeR and FeR_2 are also formed. The sensitivity was found to be 0·2 ppm, and the identification limit 0·1 μg of iron in 0·15 ml of solution. Colour development is instantaneous, with maximum colour development ensured with a 4-fold excess of reagent, and Beer's law is obeyed from 1–20 ppm. Iron(III) has been

estimated[25] in the presence of Co(II), Ni, Zn, Mn(II) and Fe(II), and the possibility of its determination in the presence of various other metal ions has been discussed.

Molybdenum. Molybdenum(VI) forms[26,27] an orange yellow water-soluble complex with the reagent in the pH range 2·8–3·7 with an absorption peak at 416 mμ. Its composition is reported to be $(MoO)R_3$. Colour development is not instantaneous but takes about 20 min, reaching a maximum with a 6-fold excess of reagent. The kinetics of this reaction were studied and the reaction found to be first-order, with specific reaction rate constant 0·1606. The sensitivity is reported to be 0·2 ppm, and Beer's law is obeyed from 1·5 to 25 ppm. Molybdenum has been estimated in the presence of the commonly associated diverse ions Cu(II), Ni, Zn, Mn(II), Co(II), UO_2(II), Ca, and W(VI).

The reagent is said to compare well with thioacetic acid, and is superior to it in having greater tolerance for W(VI).

Titanium. Titanium[28] forms a bright yellow complex with the reagent in the pH range 1·9–3·3 with an absorption peak at 405 mμ. Spectrophotometric studies suggest a 3:1 ratio of ligand to metal. Colour development is instantaneous, but a 16-fold excess of reagent is needed for maximum absorbance. To avoid reagent interference, the absorbance is measured at 425 mμ. Beer's law is obeyed from 0·3 to 2·5 ppm. Titanium has been estimated in the presence of Zn, Mn(II), Ni, Co(II), Cd, Hg(II), Mg, Be, Al and Cr(III). Cu(II), Fe(II), Fe(III), Pd(II), vanadate, phosphate, tartrate, fluoride, and tungstate interfere.

Copper, nickel, and cobalt. Spectrophotometric and conductometric studies on the complexes of copper,[29] nickel,[30] and cobalt,[31] have been reported. Copper forms a pale yellow complex with an absorption peak at 405 mμ. It is formed instantaneous and maximum absorbance occurs between pH 4·4 and 6·2. The composition is reported to be CuR_2. The yellow nickel complex has an absorption peak at 420 mμ. Optimum pH range is 3·8–5·9 and the composition is NiR_2. In this pH range the selectivity of the reagent is fairly low, so it is not very useful for the colorimetric estimation of nickel. Cobalt forms a brown complex of composition CoR_3 with an absorption peak at 390 mμ and a plateau from 450–485 mμ. The optimum pH range is 4·3–5·9 and Beer's law is obeyed over the range 0·8–10 ppm. Colour development is instantaneous and reaches a maximum for a 1:6 ratio of cobalt to reagent. Conductometric measurements suggest the formation of CoR and CoR_2 as well as CoR_3.

Fluoride, phosphate, oxalate, citrate and tartrate. The fading of the bluish black colour of the iron complex when fluoride ions are added is made the basis of an indirect spectrophotometric determination of fluoride,[32] in the concentration range 0·5–40 ppm.

The same principle has been utilized[33] for determining oxalate, phosphate, citrate and tartrate in acidic medium. Linear calibration curves are obtained only over a limited concentration range.

Metal indicator for complexometric determination of iron(III). It has recently been reported that the reagent is a good metal indicator for the direct complexometric determination of iron.[34] The colour change at the end-point from bluish black to lemon yellow or colourless is very sharp and conspicuous. Many ions do not interfere. Iron in solids, ores, cement, and dolomite has been determined complexometrically with this indicator.[35]

3-Hydroxy-1-phenyl-3-methyltriazene

This is a white compound, m.p. 69°, highly soluble in alcohol and alcohol-water mixtures. With iron(III) it forms a greenish blue water-soluble complex with absorption peaks at 400, 490 and 625 mμ, the last of which is suitable for the colorimetric determination of iron. The optimum pH range is 3·1–4·5, and Beer's law is obeyed over the range 1–10 ppm. The composition of the complex is FeR_3 and the sensitivity is 0·2 ppm. No superiority over other reagents is claimed.

Other hydroxytriazenes

3-Hydroxy-1-*p*-tolyl-3-phenyltriazene[6](I), 3-hydroxy-1-*p*-tolyl-3-methyltriazene[7](II) and 3-hydroxy-1,3-*p*-ditolyltriazene[8](III) have also been reported as reagents for palladium and copper. Compounds (I) and (III) have more favourable conversion factors than the parent compound (3-hydroxyl-1,3-diphenyltriazene). It is reported[5] that complexes formed by 3-hydroxyl-1-*o*-chlorophenyl-3-phenyltriazene and 3-hydroxy-1-*p*-carboxyphenyl-3-phenyltriazene were gelatinous in nature and not useful for analytical purposes. Hydroxytriazenes prepared from diazo anthroquinones and phenylhydroxylamine, and their colour reactions with some metals, have been reported.[37] A new hydroxytriazene, *p*-(3-hydroxy-3-phenyltriazeno)-phenyltrimethylammonium chloride has recently been reported; it is water soluble and gives coloured water-soluble complexes.[38]

Ionization constants of hydroxytriazenes and stabilities of their metal chelates

Hydroxytriazenes are very weak acids. Most of these triazenes give a yellow colour with alkali. In the case of 3-hydroxy-1,3-diphenyltriazene, for example, an absorption peak at 348 mμ in neutral or acidic medium is shifted to 393 mμ in alkaline medium. Different workers[17,39,40] have reported different values for pK, using the same spectrophotometric method. The ionization constants for a large number of hydroxytriazenes have been reported and the effect of substitution on pK values discussed.[40,41]

Stability constants of palladium, copper, nickel, zinc, and manganese chelates of various hydroxytriazenes have been determined in a 70% v/v dioxan–water mixture by Dugar[41] and Purohit *et al.*[42] The effect of substitution on the stabilities of metal chelates has also been discussed and described[43–45] and a linear correlation between pK and $\log \beta_1$ and $\log \beta_2$ has been established. The stability sequence is reported to be

$$Pd > Cu > Ni > Zn > Mn.$$

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Résumé—Une revue des applications des hydroxytriazènes comme agents chélantants en chimie analytique.

Zusammenfassung—Eine Übersicht über die Anwendungen von Hydroxytriazenen als chelierende Agentien in der analytischen Chemie wird gegeben.

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ELEKTRONISCHES RECHNEN IN DER ANALYTISCHEN CHEMIE—II*

ALGOL-PROGRAMM FÜR DIE EINFACHE VARIANZANALYSE

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Zusammenfassung—Innere Homogenität und Gesamt-Homogenität eines gruppenweise angefallenen Datenmaterials läßt sich durch die mathematisch-statistische Methode der einfachen Varianzanalyse objektiv prüfen und sicherstellen. Die bisher bekannte varianzanalytische Datenauswertung wird durch den von Nalimov vorgeschlagenen *r*-Test erweitert, wodurch auch die innere Homogenität der Einzeldaten in jeder Gruppe beurteilt werden kann. Erst der varianzanalytisch geführte Nachweis einer Homogenität gewährleistet die einwandfreie Zusammenfassung einer Vielzahl von Einzelinformationen auf die 2 für ein Untersuchungsproblem charakteristischen Kenndaten, Gesamt-Mittelwert $\bar{x}$ und die totale Varianz s^2 bzw. Standardabweichung s. Die einfache Varianzanalyse weist zwar keine schwierigen Rechenoperationen auf, ist aber bei mehr als 50 Einzeldaten bereits sehr zeitraubend und anfällig für Rechenfehler. Bei konventioneller Rechentechnik werden z.B. für 10 Gruppen mit insgesamt 100 Einzeldaten 3 bis 6 Stunden je Person benötigt, während bei elektronischer Datenverarbeitung die Resultate in weniger als 5 min anfallen. Ein geeignetes ALGOL-Programm wird mitgeteilt. Am Beispiel des Vergleiches der Resultate flammenphotometrischer Natriumbestimmungen aus 7 Laboratorien für eine gleichartige vorgegebene Glasprobe wird eine der wichtigsten Anwendungsmöglichkeiten der einfachen Varianzanalyse in der analytischen Chemie ausführlicher behandelt.

VERWENDETE BEGRIFFE UND SYMBOLE (ALGOL-SYMBOLE IN KLAMMERN)

Gesamtzahl der Untersuchungen	n (N)
Anzahl der Gruppen	k (K)
Gruppenumfänge	l_J (L)
Laufzahlen, für Gruppen	J (J)
für Einzelwerte innerhalb der Gruppen	i (I)
Einzelwerte innerhalb der Gruppen	x_i (X[I])
Gruppen-Mittelwert	$\bar{x}_J$ (XM)
Gruppen-Varianz (Standardabweichung s_J)	s_J^2 (V)
Gesamt-Mittelwert	$\bar{\bar{x}}$ (GXM)
Varianz zwischen den Gruppen	VZ (VZ)
Mittlere Varianz innerhalb der Gruppen	VI (VI)
Totale Varianz (Gesamt-Standardabweichung s)	s^2 (GV)
Integralgrenzen r der r-Verteilung für $S = 95\%$	r_J (R)
Vergleichsgröße zum r-Test	τ (TAU)
Vergleichsgröße zum F-Test	θ^2 (—)

* Teil I—*Talanta*, 1967, **14**, 61.

EINFÜHRUNG

Problemstellung

Im Rahmen der Untersuchung von Objekten und Vorgängen werden häufig mehrere Gruppen gleichartiger Untersuchungsbefunde erhalten. Zur einwandfreien Beurteilung und Zuordnung der Tatbestände und Einflüsse ist die Klärung der Frage unerläßlich, ob die Daten insgesamt einer gemeinsamen Grundgesamtheit mit definiertem Lage- und Streuungsparameter angehören oder ob die Kenndaten der k einzelnen Gruppen sich voneinander durch überzufällige Abweichungen unterscheiden. Man spricht in diesem Zusammenhang von der Homogenität bzw. Inhomogenität das Datenmaterials. Eine objektive Entscheidung ermöglicht die mathematisch-statistische Methode der Varianzanalyse.

Bei inhomogenem Datenmaterial können Gesamt-Mittelwert $\bar{x}$ und totale Varianz s^2 oder Standardabweichung s systematisch verfälscht sein und dürfen daher nicht als umfassende Kenngrößen zu dem betreffenden Problem interpretiert werden. Durch Weglassen von Gruppen mit stark abweichenden Gruppen-Kenndaten $\bar{x}_J$ und s_J und erneute varianzanalytische Durchrechnung des restlichen Datenmaterials kann eine Homogenisierung für einen Datenrest und eine Separierung von „Ausreißer"-Gruppen erreicht werden. Die mit diesem Vorgehen zwangsläufig verbundene Verkleinerung der Gruppenanzahl k und der Gesamtanzahl n der Einzeldaten bedeutet aber auch stets einen Verlust an Aussage-Sicherheit. Daher ist die weitere varianzanalytische Aufschlüsselung eines Rest-Datenmaterials mit weniger als $n/2$ Einzeldaten kaum mehr sinnvoll.

Unter den zahlreichen Möglichkeiten für die Anwendung der Varianzanalyse seien im folgenden nur einige genannt.

Zusammenfassung chronologisch angefallener Prüfbefunde (Zeiteinfluß)

Beispiel: Ermittlung der Jahres-Kenndaten aus $k = 12$ Monats-Kenndaten.

Mengenverteilungen (Prozeß- oder Herstellungseinfluß)

Beispiel: Homogenität der Verteilung eines bestimmten Stoffes nach definierten Mischprozessen bzw. Herstellbedingungen.

Trendreihen (Einflußanalyse für verschiedene Parameter)

Beispiel: Konstanz oder Änderung der Resultate von Analysengruppen bei systematischer Variation eines Zustandsparameters wie Temperatur, Druck, Volumen oder auch Konzentration zugesetzter Stoffe *etc.*

Zuverlässigkeitstest für Prüfverfahren

Beispiel: Resultatvergleich von verschiedenen Laboratorien auf der Basis einer vorgegebenen Prüfsubstanz. Für diesen wichtigen Anwendungsbereich wird abschließend ein typisches Beispiel durchgerechnet und diskutiert.

Eine Datengruppe besteht aus l_J Einzeldaten x_i in Form von gleichartigen Analysenbefunden oder auch physikalischen Merkmalsgrößen, die im allgemeinen zu einem Niveauwert $\bar{x}_J$ und einem Streuungswert s_J^2 bzw. s_J zusammengefaßt

werden können. Für k Gruppen ist danach ein k-maliger Berechnungsgang, wie folgt, durchzuführen:

$$\begin{aligned} &\text{Gruppen-Mittelwert} \qquad \bar{x}_J = \frac{1}{l_J} \sum_{1}^{l} x_i \\ &\text{Gruppen-Varianz} \qquad s_J^2 = \frac{1}{l_J - 1} \sum_{1} (x_i - \bar{x}_J)^2 \end{aligned} \tag{1}$$

wobei $i = 1, 2, \ldots, l$ Laufzahl der Einzelwerte in einer Gruppe
$J = 1, 2, \ldots, k$ Laufzahl der Gruppen (Gruppen-Nummern)
Abbildung 1 gibt einem Überblick für ein Datenmaterial von $k = 5$ Gruppen mit verschiedenem Umfang.

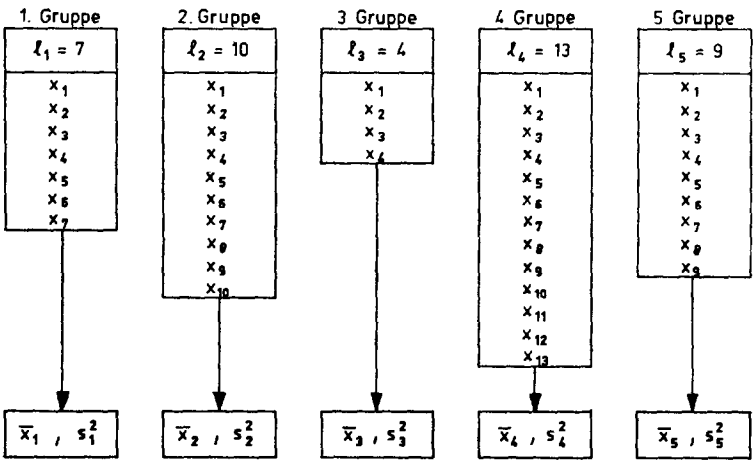

ABB. 1.—Einzeldaten, Mittelwerte und Varianzen für ein Beispiel mit $k = 5$ Gruppen.

Ein spezieller Sonderfall liegt vor, wenn zwar die Gruppen-Kenndaten l_J, $\bar{x}_J$, s_J bekannt, die Einzelwerte x_i jedoch nicht mehr zugänglich sind. Die varianzanalytische Zusammenfassung solcher Daten ist problematisch, da die oft starke Rundung der Gruppen-Kenndaten zu einer beträchtlichen Verfälschung des Endurteils führen kann. Nur bei hinreichend großer Ziffernzahl in der Angabe von $\bar{x}_J$ und s_J wird man auch für die Durchrechnung des Sonderfalles zuverlässige Endresultate erwarten dürfen. Besser ist aber in jedem Fall die Angabe und Verrechnung der Einzeldaten x_i einer jeden Gruppe. Weitere Einzelheiten zu den zweckmäßigsten Rechengängen und Datenprüfungen bringt das Kapitel über die mathematische Struktur der einfachen Varianzanalyse.

Elektronische Datenverarbeitung

Wie bereits bei der Arbeit I (Modellanalysen) werden für den Normalfall und den Sonderfall der Varianzsanalyse Rechenprogramme in der problemorientierten Universalsprache ALGOL (ALGO-rithmic L-anguage) unter Verwendung der für das Codesystem ALCOR CCIT zulässigen Zeichen formuliert. Bei Vorliegen der Programme beschränkt sich auch hier die weitere Tätigkeit des Benutzers auf die Auflistung der Untersuchungsbefunde in programmrichtiger Reihenfolge, wie dies Abb. 2 zeigt.

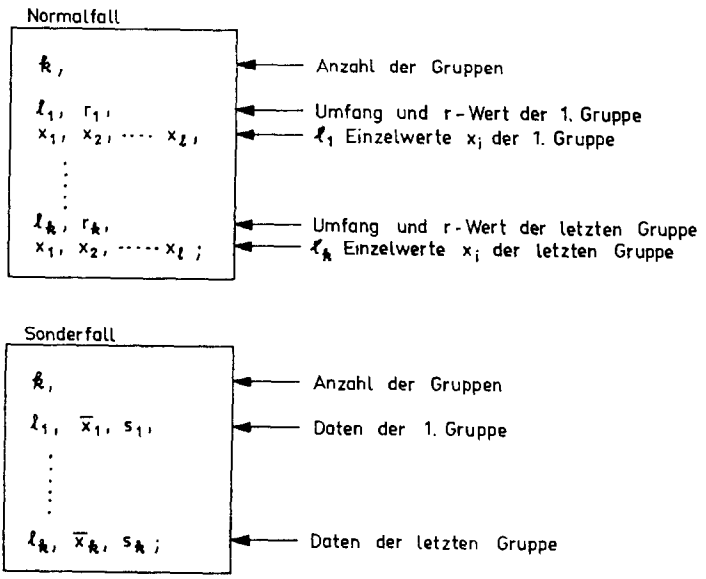

ABB. 2.—Datenlisten bei einfachen Varianzanalysen.

Weitere Einzelheiten über den Gebrauch von ALGOL siehe Arbeit I und die dort angeführte ALGOL-Literatur.

MATHEMATISCHE STRUKTUR

Rechengänge

Bei der k-maligen Gruppenrechnung ermittelt man zweckmäßig zunächst die Gruppensummen S_J der Einzelwerte x_i und QS_J der Einzelwert-quadrate x_i^2, woraus in einfacher Weise die Gruppen-Kenndaten $\bar{x}_J$, s_J^2 bzw. s_J berechnet werden können, soweit sie nicht im Sonderfall bereits vorgegeben sind. Tabelle I zeigt die Rechengänge der Gruppenrechnung.

Wie noch gezeigt wird, läßt sich die „innere" Homogenität der Daten x_i innerhalb einer jeden Gruppe durch die mathematisch-statistische Prüfmethode des r-Testes sicherstellen.

TABELLE I.—GRÖSSEN DER GRUPPENRECHNUNG

Größen		Normalfall	Sonderfall
Summe der Einzelwerte S_J =		$\sum_1^l x_i$	$l_J \cdot \bar{x}_J$
Summe der Einzelwert-Quadrate QS_J =		$\sum_1^l x_i^2$	$(l_J - 1) \cdot s_J^2 + \bar{x}_J \cdot S_J$
Mittelwert	$\bar{x}_J = XM_J$ =	$\frac{1}{l_J} \cdot S_J$	vorgegeben
Varianz	$s_J^2 = V_J$ =	$\frac{1}{l_J - 1} \{QS_J - \bar{x}_J \cdot S_J\}$	$s_J \cdot s_J$
(bzw. Standardabweichung s_J)			s_J vorgegeben

Das gesamte Datenmaterial der k-Gruppen wird danach zu einem übergeordneten Niveauwert $\bar{\bar{x}}$ und 3 Streuungswerten VZ, VI und s^2 zusammengefaßt, wobei die k Gruppensummenpaare S_J, QS_J, die Mittelwerte $\bar{x}_J$ und die Gruppenumfänge l_J in diese Gesamtrechnung eingehen, wie Tab. II zeigt.

TABELLE II.—GRÖSSEN DER GESAMTRECHNUNG

Summen	
Gesamt-Anzahl	$n = \mathrm{N} = \sum_1^l l_J$
Gesamtsumme der Einzelwerte	$GS = \sum_1^l \left\{ \sum_1^l x_i \right\} = \sum_1^l S_J$
Gesamtsumme der Einzelwert-Quadrate	$GQS = \sum_1^k \left\{ \sum_1^l x_i^2 \right\} = \sum_1^k QS_J$
Gesamtsumme des Produktes aus Gruppenmittel mal Gruppensumme	$GSQ = \sum_1^k l_J \cdot \bar{x}_J^2 = \sum_1^k \bar{x}_J \cdot S_J$
Endresultate	
Gesamt-Mittelwert	$\bar{\bar{x}} = \mathrm{GXM} = \frac{1}{n} \sum_1^k S_J = \frac{1}{n} GS$
Varianz zwischen den Gruppen	$\mathrm{VZ} = \frac{1}{k-1} \sum_1^k l_J (\bar{x}_J - \bar{\bar{x}})^2 = \frac{1}{k-1} \{GSQ - \bar{\bar{x}} \cdot GS\}$
Mittlere Varianz innerhalb der Gruppen	$\mathrm{VI} = \frac{1}{n-k} \sum_1^k (l_J - 1) \cdot s_J^2 = \frac{1}{n-k} \{GQS - GSQ\}$
Totale Varianz (bzw. Standardabweichung s)	$s^2 = \mathrm{GV} = \frac{1}{n-1} \{(k-1) \cdot \mathrm{VZ} + (n-k) \cdot \mathrm{VI}\}$
	$= \frac{1}{n-1} \{GQS - \bar{\bar{x}} \cdot GS\}$

Zur Prüfung des gesamten Datenmaterials auf Homogenität wird abschließend ein F-Test durchgeführt.

Prüfung der Gruppen-Homogenität durch den t-*Test*

Die Gruppen-Kenndaten $\bar{x}_J$ und s_J bzw. s_J^2 sind nur dann einwandfreie Gruppengrößen, wenn keiner der Einzelwerte x_i innerhalb der betreffenden Gruppe extrem weit vom Mittelwert abweicht. Die „innere" Homogenität der Gruppendaten x_i kann durch den r-Test[1,2] überprüft und sichergestellt werden. Hierzu bildet man für den kleinsten und größten x_i-Wert und eventuellen weiteren stark vom Mittelwert abweichenden x_i-Werten die Prüfgröße:

$$\tau_i = \frac{|x_i - \bar{x}_J|}{s_J} \sqrt{\frac{l_J}{l_J - 1}} \tag{2}$$

Mit den Integralgrenzen r der r-Verteilung wird τ_i verglichen, wobei für die jeweilige numerische Größe von $r = r_J$ der vom Gruppenumfang l_J abhängige Freiheitsgrad $f = l_J - 2$ und die Statistische Sicherheit $S = 95\%$ oder $S = 99\%$ (Level of significance 0,05 bzw. 0,01) maßgebend ist. Als Funktion von f und S ist r tabelliert.[1,2] Theoretisch kann $\tau_i \geqq r(95)$ 1-Mal unter 20 Werten x_i und $\tau_i \geqq r(99)$ sogar nur 1-Mal unter 100 Werten erwartet werden. Die Gruppendaten sind praktisch als in sich homogen zu beurteilen, wenn bei $l_J = 10$ bis 20 1-Mal, bei $l_J = 21$ bis 40 2-Mal, bei $l_J = 41$ bis 60 3-Mal Prüfgrößen $\tau_i \geqq r(95)$ gefunden werden. Praktisch ist $\tau_i \geqq r(99)$ 1-Mal für $l_J = 50$ bis 100 zulässig.

Für $l_J = 10$ entnimmt man z.B. der Tabelle für $f = 8$ die r-Werte:

$$r(95) = 1{,}895 \qquad \text{und} \qquad r(99) = 2{,}294$$

Eine homogene Datengruppe liegt in diesem Fall dann vor, wenn höchstens 1-Mal $\tau_i \geqq r(95) = 1{,}895$ vorkommt. Bei mehreren Befunden $\tau_i \geqq r(95)$ oder sogar solche mit $\tau_i \geqq r(99)$ sind die betreffenden x_i-Werte als „Ausreißer" einzustufen. Die varianzanalytischen Berechnungen müssen sodann unter Fortlassen der Ausreißer wiederholt werden. Darüber hinaus sollte man bemüht sein, die Ursachen für Ausreißer aufzudecken. Der r-Test setzt die Kenntnis der Einzelwerte x_i voraus. Liegen im Sonderfall nur die Gruppendaten l_J, $\bar{x}_J$, s_J vor, so kann auf innere Homogenität nicht geprüft werden, wodurch eine erhöhte Gefahr der systematischen Resultatverfälschung resultiert.

Für die Praxis ist eine umgeformte Beziehung (2) einfacher zu handhaben. Mit $\tau_i \geqq r_J$ folgt:

$$| x_i - \bar{x}_J | \geqq r_J \cdot s_J \sqrt{\frac{l_J - 1}{l_J}} = r_J \sqrt{\frac{(l_J - 1) \cdot V_J}{l_J}} = PG \tag{3}$$

Wenn der absolute Differenzbetrag $(x_i - \bar{x}_J)$ gleich oder größer als eine aus l_J, $r_J(S)$, s_J bzw. V_J gebildeten Prüfgröße PG ist, so liegt eine Überschreitung der vorgegebenen r-Grenze vor. Das Normalprogramm enthält den r-Test und druckt für externe Vergleiche die Versuchsnummer i = I, den betreffenden Wert x_i = X[I], die Größe τ_i = TAU und den Wert r_J = R[J] aus, wenn die $r(95)$- Grenze überschritten wird.

Prüfung der Gesamt-Homogenität durch den F-*Test*

Die Homogenität des gesamten Datenmaterials wird durch einen F-Test[1–4] geprüft und beurteilt. Die einfache Prüfgröße

$$\theta^2 = \frac{VZ}{VI} \tag{4}$$

ist hierzu lediglich mit den Integralgrenzen F der F-Verteilung für die Freiheitsgrade

$$\text{von } VZ, \text{ d.h. } f_1 = k - 1 \text{ und}$$

$$\text{von } VI, \text{ d.h. } f_2 = n - k$$

sowie vorgegebenen Statistischen Sicherheiten $S = 95/99/99{,}9\%$ (Level of significance 0,05/0,01/0,001) zu vergleichen.

Die F-Werte sind als Funktion von f_1, f_2 und S tabelliert,[1–4] doch muß eventuell

interpoliert werden. Wegen $F \leqq 1$ zeigt eine Prüfgröße $\theta^2 \leqq 1$ auch ohne Vergleich mit den F-Werten stets ein streng homogenes Datenmaterial an. In allen Fällen $\theta^2 > 1$ urteilt man zweckmäßig, wie folgt:[2]

$$\theta^2 < F(95): \quad \text{streng homogen}$$

$$F(95) \leqq \theta^2 < F(99): \quad \text{homogen}$$

$$F(99) \leqq \theta^2 < F(99{,}9): \quad \text{nahezu homogen}$$

$$\theta^2 \geqq F(99{,}9): \quad \text{inhomogen}$$

Nur für $\theta^2 < F(99{,}9)$, bei strengen Maßstäben sogar für $\theta^2 < F(95)$, stellen Mittelwert $\bar{x}$, totale Varianz s^2 bzw. Standardabweichung s eine zulässige auf nur 2 Kenndaten konzentrierte Information zu dem betreffenden Problem dar.

In einem inhomogenen Datenmaterial sind dagegen überzufällige Einflüsse wirksam. Wie bereits in der Einführung beschrieben, kann durch Fortlassen von Gruppen mit stark abweichenden Gruppenkenndaten $\bar{x}_J$, s_J^2 bzw. s_J und erneute Rechnung eine Homogenität der Restdaten und eine Separierung von Ausreißer-Gruppen erreicht werden.

Im nachfolgend angeführten Normal- und Sonderprogramm wird lediglich θ^2 berechnet und ausgedruckt, während der Vergleich mit F-Werten extern erfolgen muß. Dies erspart in vielen Fällen eine zeitraubende Interpolationsrechnung für nicht tabellierte F-Werte und ermöglicht eine eventuelle andere Abstufung des Urteils.

PROGRAMMIERUNG

Flußdiagramm

Abbildung 3 zeigt das vollständige Ablaufschema der einfachen Varianzanalyse für den Normalfall. Die Gruppenrechnung wird nur 1-Mal formuliert und so dann in einem k-maligen Zyklus durchgeführt. Dieses Vorgehen erspart die Indizierung durch die Gruppen-Nummer J. Es kann $l_J = \mathrm{L}$, $r_J = \mathrm{R}$ und $x_{iJ} = \mathrm{X[I]}$ gesetzt werden. Die richtige Auflistung der Eingangsdaten für den Normalfall zeigt Abb. 2.

Im Sonderfall der einfachen Varianzanalyse mit vorgegebenen Gruppendaten $l_J, \bar{x}_J, s_J$ beschränkt sich der k-Zyklus auf das Einlesen dieser Größen, wobei auch hier $l_J = \mathrm{L}$, $\bar{x}_J = \mathrm{XM}$, $s_J = SJ$ gesetzt werden kann. Es sei ausdrücklich darauf hingewiesen, daß die elektronische Rechnung für den Sonderfall gegenüber einer konventionellen Rechentechnik nur dann merkliche zeitliche und sonstige Vorteile besitzt, wenn mindestens 10 Gruppen zusammenzufassen sind.

ALGOL-Programm

Die relativ kurzen und einfachen ALGOL-Programme für den Normalfall und den Sonderfall sind in den Tabellen III und IV zusammengestellt.

Die Programme sind erprobt und brauchen von einem Benutzer nur sorgfältig abgeschrieben und an ein Rechenzentrum gegeben zu werden: Die zukünftige Arbeit beschränkt sich sodann auf die Auflistung der Befunde in programmrichtiger Reihenfolge nach Abb. 2.

Weitere Hinweise zur ALGOL-Programmierung wurden in Arbeit I gebracht, in der auch ausführlichere ALGOL-Literatur angegeben wird.

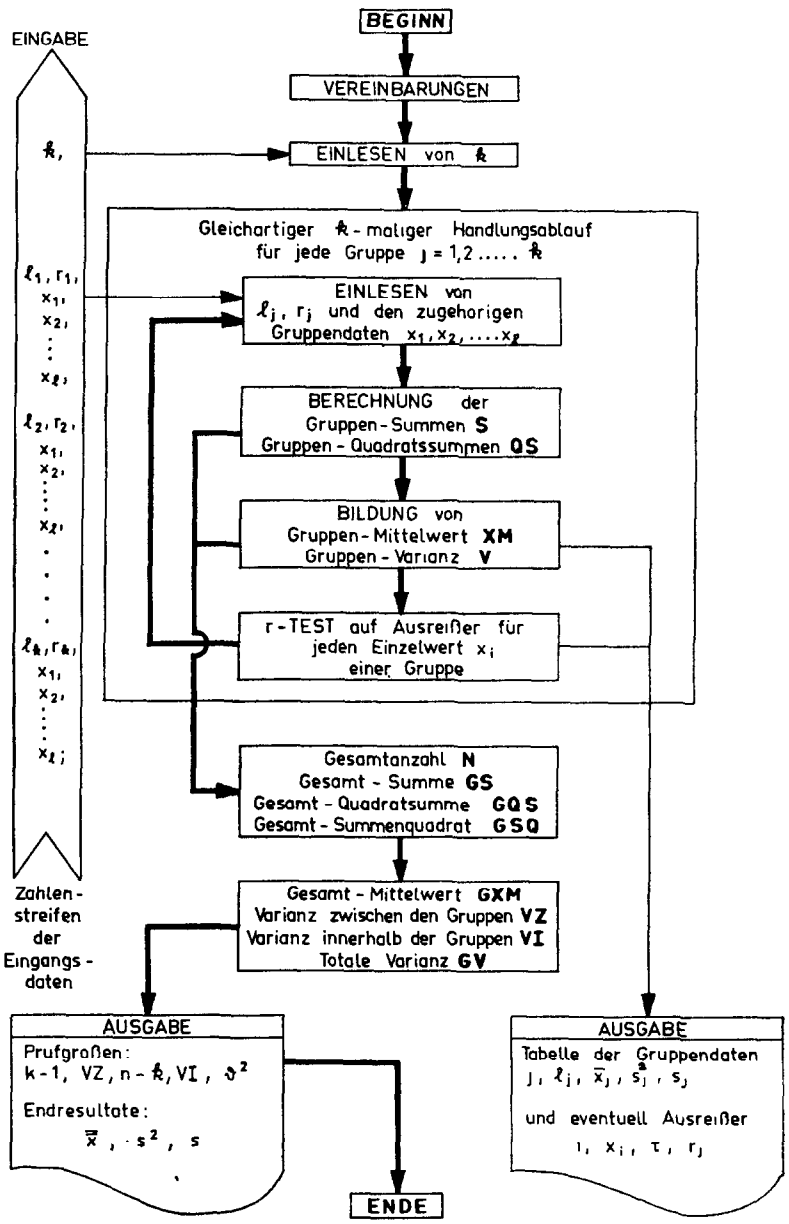

ABB. 3.—Ablaufschema der einfachen Varianzanalyse.

TABELLE III.—ALGOL-PROGRAMM FÜR DEN NORMAFALL DER EINFACHEN VARIANZANALYSE

```
'BEGIN' 'COMMENT' EINFACHE VARIANZANALYSE;
  'REAL' GS, GQS, GSQ, R, S, QS, XM, V, PG, TAU, VZ, VI GXM, GV;
  'INTEGER' K, N, J, L, I;
  READ (K);
  WRITE ("<≡EINFACHE ␣ VARIANZANALYSE, GRUPPEN ␣ K ="); TYPE (K);
  WRITE ("<≡≡GRUPPE 8␣J 16␣L 8␣XM 15␣V 15␣SJ");

  GS: = GQS: = GSQ: = N: = o;
  'FOR' J: = 1 'STEP' 1 'UNTIL' K 'DO'
   'BEGIN' READ (L, R);
    'BEGIN' 'ARRAY' X [1:L];
     S: = QS: = o;
     'FOR' I: = 1 'STEP' 1 'UNTIL' L 'DO' 'BEGIN'
      READ (X[I]); S: = S + X[I];
      QS: = QS + X[I] × X[I]; 'END' GRUPPENSUMMEN;

      XM: = S/L;
        V: = (QS − S × XM)/(L − 1);
       PG: = R × SQRT ((L − 1) × V/L);
       PRINT (J, L, XM, V, SQRT (V));
      'FOR' I: = 1 'STEP' 1 'UNTIL' L 'DO' 'BEGIN'
       'IF' ABS (X[I] − XM) 'NOT LESS' PG 'THEN' 'BEGIN'
        TAU: = ABS (X[I]-XM) × R/PG;
        WRITE ("<≡R − TEST: 7␣I 7␣X[I] 13␣TAU 15␣R");
        PRINT (I, X[I], TAU, R); 'END' AUSGABE 'END' R-TEST;

      N: = N + L;
     GS: = GS + S;
    GQS: = GQS + QS;
    GSQ: = GSQ + S × XM;
    'END' X-FELD;
   'END' SUMMIEREN;

  GXM: = GS/N;
    VZ: = (GSQ − GS × GXM)/(K − 1);
    VI: = (GQS − GSQ)/(N − K);
    GV: = (GQS − GS × GXM)/(N − 1);

  WRITE ("<≡≡≡PRUEFGROESSEN: <≡11␣F1 = K − 1 6␣VZ 19␣F2 =
                                          N − K 7␣VI 10␣THETA-QUADRAT");
  PRINT (K − 1, VZ, N − K, VI, VZ/VI);
  WRITE ("<≡≡≡ENDRESULTATE: <≡14␣N 7␣GXM 15␣GV 15␣S");
  PRINT (N, GXM, GV, SQRT (GV));

'END' PROGRAMM FUER EINFACHE VARIANZANALYSE
```

BEISPIEL

Das nachfolgende Beispiel wurde an einer relativ kleinen und langsamen Rechenanlage ZUSE 23 gerechnet. Der Zeitbedarf für das einmalige Einlesen des ALGOL-Programmes beträgt für den Normalfall 2 Minuten und für den Sonderfall 1 Minute. Für das Einlesen des Zahlenstreifens der Eingangsdaten sowie für Rechnung und Resultatausgabe werden weitere 3 bzw. 1,5 Minuten benötigt. Das direkte Ausdrucken der Resultate in Klarschrift beansprucht bei den hier formulierten Programmen etwa 75 % der Zeit, da bei der Z 23 die Rechenvorgänge während des Druckvorganges unterbrochen werden. Bei einer größeren Anzahl zu verarbeitender Zahlenstreifen ist es daher vorteilhafter, die Resultate nicht in Klarschrift sondern zunächst in der

TABELLE IV.—ALGOL-PROGRAMM FÜR DEN SONDERFALL DER EINFACHEN VARIANZANALYSE

```
'BEGIN' 'COMMENT' EINFACHE VARIANZANALYSE, SONDERFALL;

  'REAL' GS, GQS, GSQ, XM, SJ, S, GXM, VZ, VI, GV;
  'INTEGER' K, N, L, J;

  READ (K);

  WRITE (" <≡ EINFACHE ␣ VARIANZANALYSE, SONDERFALL ␣ K = ");
    TYPE (K);

  GS: = GQS: = GSQ: = N: = 0;
   'FOR' J: = 1 'STEP' 1 'UNTIL' K 'DO'
    'BEGIN' READ (L, XM, SJ);
       S: = L × XM;
       N: = N + L;
      GS: = GS + S;
     GQS: = GQS + (L − 1) × SJ × SJ + XM × S;
     GSQ: = GSQ + XM × S;
    'END' SUMMIEREN;

    GXM: = GS/N;
      VZ: = (GSQ − GS × GXM)/(K − 1);
      VI: = (GQS − GSQ)/(N − K);
      GV: = (GQS − GS × GXM)/(N − 1);

  WRITE (" <≡≡ PRUEFGROESSEN: <≡ ␣11 F1 = K − 1 ␣6 VZ ␣19 F2 =
                                  N − K ␣7 VI ␣10 THETA-QUADRAT");
  PRINT (K − 1, VZ, N − K, VI, VZ/VI);
  WRITE (" <≡≡ ENDRESULTATE: <≡ ␣14 GXM ␣15 GV ␣15 S");
  PRINT (N, GXM, GV, SQRT (GV));

'END' PROGRAMM FUER EINFACHE VARIANZANALYSE, SONDERFALL
```

sehr viel schnelleren Lochstreifenform ausgeben zu lassen. Die Lochstreifen können später über einen ALGOL-Schreiber in beliebig viele Klarschriftexemplare umgesetzt werden.

Zielsetzung: Überprüfung der Zuverlässigkeit und Ermittlung der Standardabweichung eines flammenphotometrischen Prüfverfahrens für Natriumgehalte zwischen 1,0 bis 2,0 Gew% in einem häufig verwendeten Glastyp.

Teilnehmer: 7 Laboratorien.

Vorbereitung: Durch eine neutrale, hinsichtlich der Auswertung federführende Institution wird eine 1000-g Großprobe eines typischen Glases auf eine Korngröße von weniger als 60 μ vermahlen und sorgfältig homogenisiert. Jedem Laboratorium wird eine Kleinprobe von 20 g in gut verschlossener Kunststoff-Pulverflasche übersandt.

Auflagen: Jedes Laboratorium (Gruppe) hat mindestens $l_J = 6$ flammenphotometrische Bestimmungen durchzuführen, wobei der erforderliche Abrauchprozeß je Bestimmung mit Einwaagen im Bereich $G = 100$ bis 500 mg erfolgen soll. Eine Probenteilung des gelösten Rückstandes wird ebenso wie Arbeitstechnik und

benutztes Gerät freigestellt. Von den Laboratorien sind die Einzelergebnisse $x_i = H_i$ in Gew% Na auf 2 Stellen nach dem Komma sowie die jeweils verwendeten Arbeitsvorschriften (Einwaagen, Reagentien, Aufschlußtechnik, Probenteilung, Art des Gerätes) mitzuteilen.

Die erhaltene Resultatmatrix zeigt Tab. V, die allen beteiligten Laboratorien mit den Ergebnissen der varianzanalytischen Auswertung nach Abschluß der Untersuchungen zugestellt wird. Sind an dem Versuch Laboratorien verschiedener Firmen, Institute oder sonstige Untersuchungsstellen beteiligt, so ist aus gewichtigen sachlichen und psychologischen Gründen von der neutralen Stelle unbedingt eine anonyme Aufschlüsselung und Bewertung durchzuführen. Hierzu werden den beteiligten Laboratorien willkürlich Gruppennummern zugeordnet. Jedes Laboratorium erhält neben den Endunterlagen nur seine eigene Nummer, nicht aber die Nummern der anderen Laboratorien. Bei diesem Vorgehen wird man gewisse berechtigte Vorurteile gegen solche für den Fortschritt der analytischen Prüftechnik sehr wertvolle Ringsversuche vermeiden können. Neben den Einzelresultaten H_i enthält Tab. V auch die aus Tabellen[1,2] entnommenen r-Werte für $S = 95$ und 99% Statistischer Sicherheit.

TABELLE V.—EINZELWERTE $x_i = H_i$ IN GEW.% Na AUS 7 LABORATORIEN

Laboratorium (Gruppe)		1	2	3	4	5	6	7
Gruppendaten	H_1	1,57	1,68	1,46	1,63	1,70	1,52	1,57
	H_2	1,71	1,59	1,49	1,58	1,69	1,60	1,54
	H_3	1,64	1,51	1,55	1,59	1,72	1,54	1,65
	H_4	1,66	1,62	1,41	1,60	1,77	1,62	1,61
	H_5	1,61	1,65	1,48	1,53	1,73	1,68	1,59
	H_6	1,72	1,49	1,50	1,55	1,65	1,58	1,53
	H_7		1,63		1,61	1,68		1,59
	H_8					1,75		1,67
	H_9					1,70		
	H_{10}					1,76		
Gruppenumfang l_j		6	7	6	7	10	6	8
Prüfgröße r_j (95)		1,814	1,848	1,814	1,848	1,895	1,814	1,870
r_j (99)		2,051	2,142	2,051	2,142	2,294	2,051	2,208

Die Daten der Tab. V wurden nach Abb. 2 aufgelistet und unter Verwendung des Normal-Programmes durchgerechnet. Tabelle VI zeigt das erhaltene Resultatbild in Klarschrift.

1. Urteil: Wichtigste Größe ist zunächst das gefundene $\theta^2 = 14{,}807$. F-Werte mit dem Freiheitsgrad $f_1 = 6$ und $f_2 = 43$ sind im allgemeinen nicht tabelliert. Doch zeigt bereits der benachbarte Wert

$$F\{f_1 = 6, f_2' = 40,\ S = 99{,}9\%\} = 4{,}73 < \theta^2$$

daß das gesamte Datenmaterial als eindeutig inhomogen zu beurteilen ist. Die Tabelle der Gruppendaten wird nicht durch Ausgabe von r-Testwerten unterbrochen, so daß alle Gruppen in sich homogen sind. Gruppe 3 weist mit $\bar{H}_3 = 1{,}482$ Gew% Na den Kleinsten und Gruppe 5 mit $\bar{H}_5 = 1{,}715$ Gew% Na den höchsten Gruppen-Mittelwert auf.

TABLE VI.—KLARSCHRIFTBILD DER VARIANZANALYSE FUR ALLE $K = 7$ GRUPPEN

ALCORA ZUSE Z 23 MODUS 4
EINFACHE VARIANZANALYSE, GRUPPEN K = 7

GRUPPE	J	L	XM	V	SJ
	1	6	$.165166666_{10}1$	$.333666801_{10}-2$	$.577638988_{10}-1$
	2	7	$.159571428_{10}1$	$.506191452_{10}-2$	$.711471328_{10}-1$
	3	6	$.148166666_{10}1$	$.213667154_{10}-2$	$.462241445_{10}-1$
	4	7	$.158428571_{10}1$	$.119523704_{10}-2$	$.345722000_{10}-1$
	5	10	$.171500000_{10}1$	$.114999557_{10}-2$	$.380788073_{10}-1$
	6	6	$.158999999_{10}1$	$.332000553_{10}-2$	$.576194891_{10}-1$
	7	8	$.159375000_{10}1$	$.239821416_{10}-2$	$.489715648_{10}-1$

PRUEFGROESSEN:

F1 = K − 1	VZ	F2 = N − K	VI	THETA-QUADRAT
6	$.383421579_{10}-1$	43	$.258946418_{10}-2$	$.148069852_{10}2$

ENDRESULTATE:

N	GXM	GV	S
50	$.161000000_{10}1$	$.696734505_{10}-2$	$.834706238_{10}-1$

TABELLE VII.—TEILE DER KLARSCHRIFTBILDER DER FOLGERECHNUNGEN

Rechnung ohne Gruppe 3 (K = 6)

.
.
.

PRUEFGROESSEN:

F1 = K − 1	VZ	F2 = N − K	VI	THETA-QUADRAT
5	$.235522508_{10}-1$	38	$.264904687_{10}-2$	$.889083961_{10}1$

ENDRESULTATE:

N	GXM	GV	S
44	$.162750000_{10}1$	$.507965198_{10}-2$	$.712716773_{10}-1$

Rechnung ohne Gruppe 5 (K = 6)

.
.
.

PRUEFGROESSEN:

F1 = K − 1	VZ	F2 = N − K	VI	THETA-QUADRAT
5	$.184480667_{10}-1$	34	$.289109173_{10}-2$	$.638100356_{10}1$

ENDRESULTATE:

N	GXM	GV	S
40	$.158375000_{10}1$	$.488557570_{10}-2$	$.698968933_{10}-1$

Rechnung ohne Gruppen 3 und 5 ($K = 5$)

.
.
.

PRUEFGROESSEN:

F1 = K − 1	VZ	F2 = N − K	VI	THETA-QUADRAT
4	$.467008352_{10}-2$	29	$.302116624_{10}-2$	$.154578833_{10}1$

ENDRESULTATE:

N	GXM	GV	S
34	$.160176470_{10}1$	$.322103500_{10}-2$	$.567541628_{10}-1$

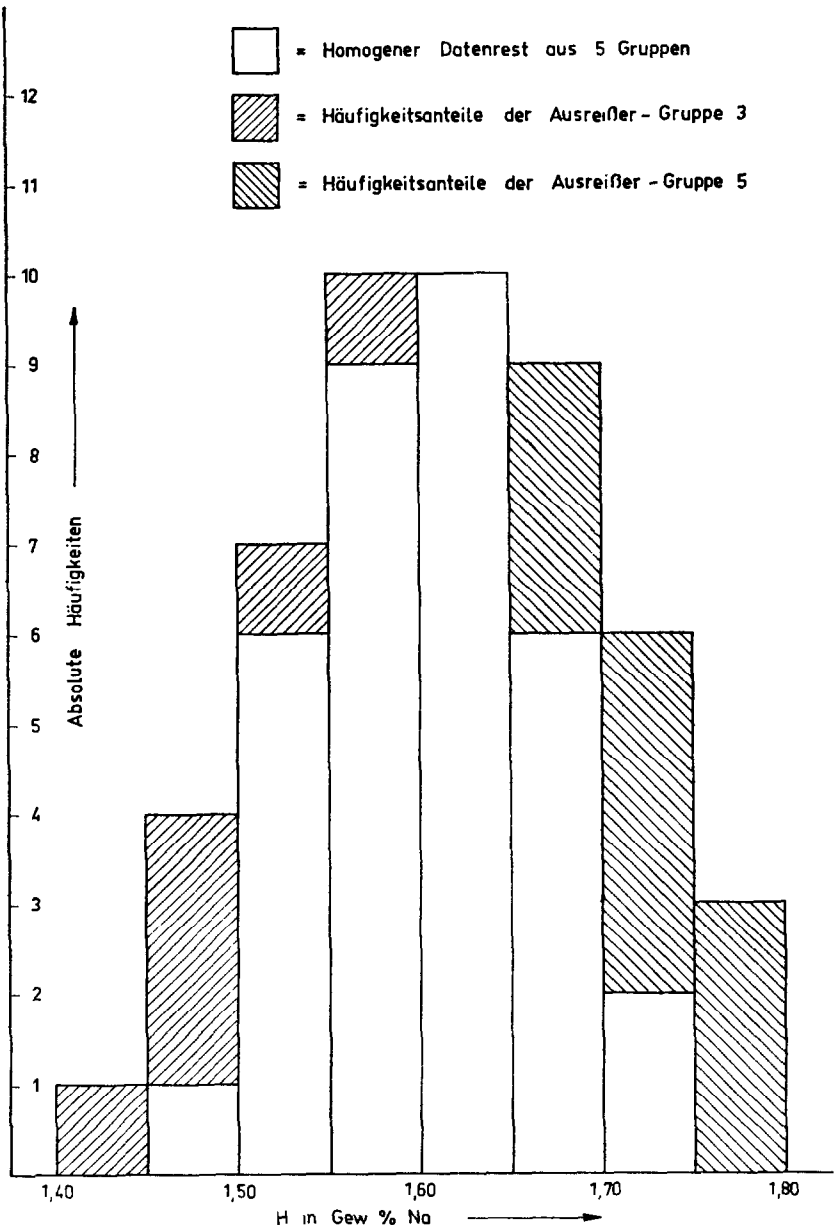

Abb. 4.—Histogramm der absoluten Häufigkeiten für die Klassenbreite $\Delta H = 0{,}05$ Gew.% Na.

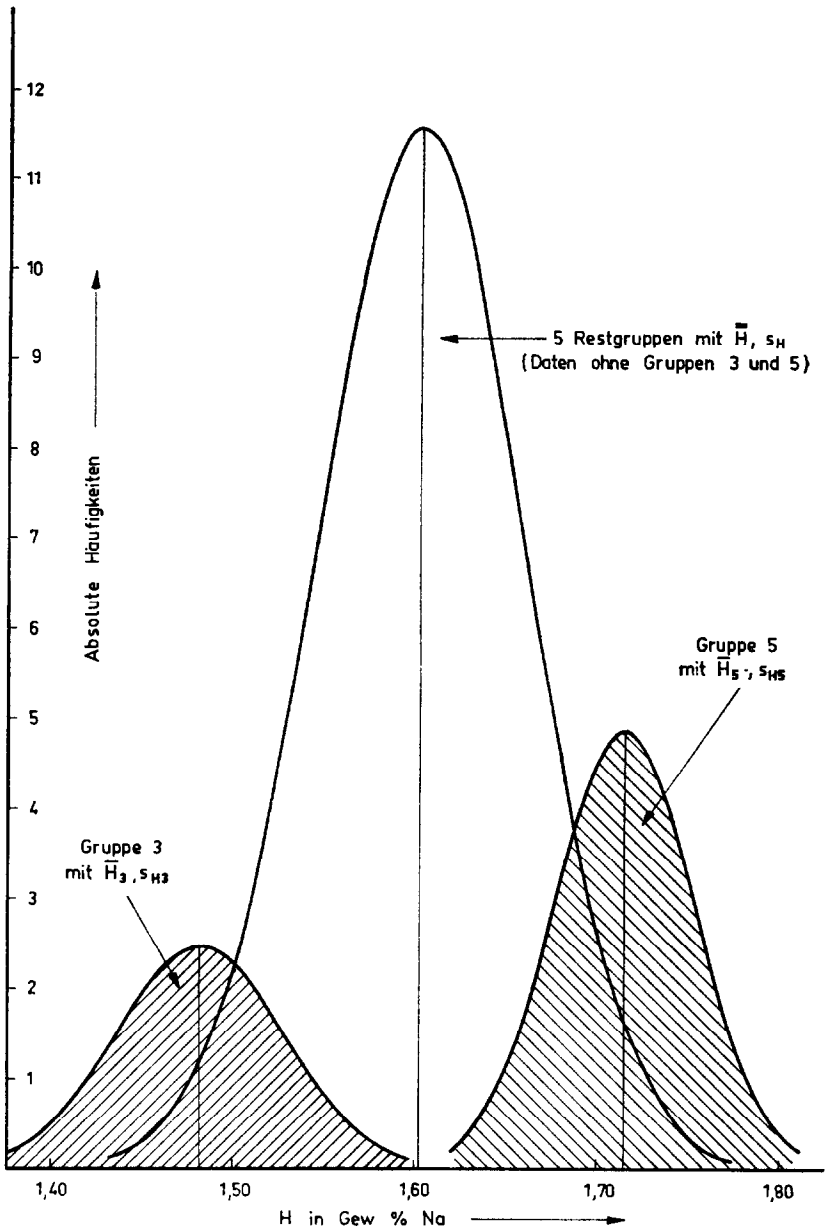

ABB. 5.—Homogener Datenrest und Ausreißer-Gruppen als Normalverteilungen mit Schätzwerten H, s_H.

Auf Grund des 1. Urteils wurden erneute Rechnungen unter Fortlassen der Gruppe 3 bzw. der Gruppe 5 bzw. der Gruppen 3 und 5 durchgeführt. Tabelle VII zeigt die Teile: Prüfgrößen und Endresultate der betreffenden Klarschriftbilder. Die Gruppen-Kenndaten bleiben naturgemäß unverändert.

Zwischenurteile: Ohne Gruppe 3 wird $\theta^2 = 8{,}891$ ($f_1 = 5$, $f_2 = 38$) und ohne Gruppe 5 $\theta^2 = 6{,}381$ ($f_1 = 5$, $f_2 = 34$) erhalten. Bereits der Näherungswert

$$F\{f_1 = 5, f_2' = 30, S = 99{,}9\,\%\} = 5{,}53 < \theta^2$$

zeigt, daß das jeweilige Restmaterial nach wie vor inhomogen ist. Der kleinere θ^2-Wert bei Fortlassen der Gruppe 5 läßt darauf schließen, daß Gruppe 5 einen größeren Einfluß hinsichtlich der Inhomogenität besitzt als Gruppe 3.

Endurteil: Ohne Gruppe 3 und 5 resultiert

$$\theta^2 = 1{,}546 < F\{f_1 = 4, f_2 = 29, S = 95\,\%\} = 2{,}70$$

das heißt ein „streng homogenes" Datenmaterial mit den Gesamt-Kenndaten:

$$\begin{aligned} \bar{\bar{H}} &= \ \ 1{,}602 \text{ Gew\% Na} \\ s_H &= \pm 0{,}057 \text{ Gew\% Na} \\ (VK &= \pm 3{,}54 \ \text{Rel\%}) \end{aligned}$$

Den Einfluß der Inhomogenität erkennt man an den bisherigen Gesamtdaten:

alle Gruppen: $\bar{\bar{H}} = \ \ 1{,}610$ Gew% Na, $s_H = \pm 0{,}083$ Gew% Na, (VK $= \pm 5{,}18$ Rel%)

ohne Gruppe 3: $\bar{\bar{H}} = \ \ 1{,}628$ Gew% Na, $s_H = \pm 0{,}071$ Gew% Na, (VK $= \pm 4{,}38$ Rel%)

ohne Gruppe 5: $\bar{\bar{H}} = \ \ 1{,}584$ Gew% Na, $s_H = \pm 0{,}070$ Gew% Na, (VK $= \pm 4{,}41$ Rel%)

Die Resultate der Laboratorien 3 und 5 mit

$$\bar{H}_3 = 1{,}482 \text{ bzw. } \bar{H}_5 = 1{,}715 \text{ Gew\% Na}$$

sind nach der varianzanalytischen Aufschlüsselung eindeutig zu niedrig bzw. zu hoch.

Abschließend zeigen die Abbildungen 4 und 5 die Verteilung der absoluten Häufigkeiten und die mit den Schätzwerten $\bar{H}$ und s_H resultierenden Normalverteilungen.

Summary—The homogeneity within and between groups of data can be objectively tested and established by a simple analysis of variance. The analysis of variance methods already known can be extended by means of the *r*-test proposed by Nalimov, whereby the homogeneity of single values in each group can be assessed. Only the proof of homogeneity obtained by analysis of variance guarantees the unequivocal interpretation of a large number of single results from the two characteristic

parameters—the variance s^2 (or the standard deviation s) and the mean value $\bar{\bar{x}}$. Certainly simple analysis of variance requires no difficult calculations, but, even with only 50 results to be used, is time-consuming and subject to arithmetical slips. For example, by conventional calculation methods 3–6 hr are needed for one person to handle groups containing 100 results, whereas the results can be obtained in 5 min with an electronic computer. A suitable ALGOL programme is given, and as an example of use of this potentially important application of analysis of variance, a detailed comparison is made of the flame photometric determination of sodium in a homogeneous glass sample by 7 laboratories.

Résumé—On peut objectivement examiner et établir l'homogénéité à l'intérieur et entre des groupes de données par une analyse simple de la variance. Les méthodes d'analyse de variance déjà connues peuvent être étendues au moyen de l'essai-*r* proposé par Nalimov, par lequel l'homogénéité de valeurs isolées de chaque groupe peut être appréciée. Seule la preuve d'homogénéité obtenue par l'analyse de la variance garantit l'interprétation non équivoque d'un grand nombre de résultats simples à partir des deux paramètres caractéristiques de la variance, s^2 (ou l'écart type s) et la valeur moyenne $\bar{\bar{x}}$. L'analyse simple de la variance n'exige certainement pas de calculs difficiles mais, même avec seulement 50 résultats à utiliser, elle prend beaucoup de temps et est sujette à des erreurs arithmétiques par inadvertance. Par exemple, par les méthodes de calcul ordinaires, une personne nécessite 3–6 h pour traiter des groupes contenant 100 résultats, alors que les résultats peuvent être obtenus en 5 mn avec un calculateur électronique. On donne un programme ALGOL appropriéet, comme exemple d'emploi de cette application potentiellement importante de l'analyse de la variance, on procède à une comparaison détaillée du dosage photométrique de flamme du sodium dans un échantillon de verre homogène effectué par 7 laboratoires.

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PURITY DETERMINATIONS BY DIFFERENTIAL THERMAL ANALYSIS*

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Summary—Measurement of the melting-point depression of impure samples was compared with a differential method that involved running the impure sample against a pure sample of the same material. Samples of highly purified benzophenone to which had been added known quantities of 4-methylbenzophenone were studied. The area under the curve was proportional to the difference in purity between the sample and reference material over the range studied, 0·3–2·0 mole % with a standard deviation of 0·10 mole %, an uncertainty only half as large as one obtained by the melting-point depression method with the same apparatus.

THERE is no shortage of methods capable of determining low levels of one component in another. When the impurity is similar to the major component, the most common method of analysis is based on melting-point depression.[1] In a study at the National Bureau of Standards,[2] 0·004 mole % of heptane in benzene was determined with a standard deviation of 0·0004 mole % by use of freezing and melting curves. That approach is very sensitive but also extremely slow and tedious, requiring 4 hr or more for analysis of a single sample.

The work described in this paper was begun in the hope that the application of a differential thermal technique[3,4] might shorten the time required without appreciable loss in sensitivity.‡ Our results fell far short of the desired sensitivity but did prove to be more precise than the method based upon visual observation of the melting-point depression. This paper reports the results of our comparison of two methods of purity determination by differential thermal techniques. One method involved a conventional differential thermal analysis (DTA) technique to determine the melting-point depression. The second method used the area under a curve obtained by comparing the temperature of the sample with that of an active reference sample of pure material.[3] Highly purified benzophenone diluted with carborundum was used as the reference material; benzophenone mixed with known quantities of 4-methylbenzophenone and diluted with carborundum was used as the sample. The resulting curve had a second-derivative shape, the area of which depended on the degree of overlap of the sample and reference transitions, which in turn depended on the difference in purity of the sample and reference materials.

EXPERIMENTAL

Apparatus

The DTA instrument used in this work was similar to that of Barrall and Rogers,[4] except that a more convenient method of thermocouple mounting was devised which permitted the thermocouples

* Taken in part from the Ph.D. thesis of P. B. Bowman, Purdue University, Lafayette, Indiana, August, 1965.

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‡ After submission of this manuscript, a similar procedure was reported based on use of a Perkin–Elmer Differential Scanning Calorimeter. See A. P. Gray, Thermal Analysis Newsletter, No 5. Perkin–Elmer Corporation, Norwalk, Connecticut, 1966.

to be removed from the cells without breaking the connections to the amplifier leads at the Jones terminal board. The thermocouple was mounted in an aluminium plug which served to centre it in the sample compartment. The plug was held in place by a brass compression fitting which also sealed the cell compartment. The thermocouple leads from the block to the terminal board, and all connections on the board itself, were wrapped in glass wool.

The thermocouples were Chromel/Alumel Part No. 900301 from the Instrument Products Division of E. I. DuPont de Nemours and Co., Inc. and were designed for use with the DuPont 900 DTA instrument. These thermocouples were sealed in the plugs with ceramic cement.

Two thermocouple arrangements, both with the cold junction in an ice-bath, were used in this study. For melting-point depression experiments, which involved direct measurement of temperature, the thermocouple in the sample cell was used in the circuits for both temperature and differential temperature measurements.[5] With that arrangement, the abscissa was the temperature of the sample, and there was very little variation of peak shape with purity.

For the differential measurements against pure benzophenone, one thermocouple pair detected the difference in sample and reference temperatures, while a second pair measured the block temperature. The hot junction of the latter temperature-sensing pair was located in pure carborundum in a third cell compartment. For that configuration, the abscissa of the recorder trace was the temperature of the block, and endotherms for the sample and reference cells had the same shape although the deflections were in opposite directions. Using that thermocouple arrangement, the shape of the endotherm depended on the purity of the sample. The melting of a high purity sample was completed in a narrow temperature range and had a deep endotherm. The less pure samples melted over wider temperature ranges with correspondingly shallower endotherms.

The block was non-inductively wrapped with 18-gauge asbestos-insulated nichrome wire. A 1-pint Dewar flask was placed round the block during runs. The block temperature was controlled with an F and M model 40 Linear Temperature Programmer. All runs were performed at a heating rate of 2·9°/min. The differential temperature signal was amplified by a Leeds and Northrup 9835B Stabilized d.c. (zero centre) Microvolt Indicating Amplifier. Part of the temperature signal was bucked out (backed off) by a bridge-type bucking source.[6] The remainder was fed to another Leeds and Northrup amplifier. The thermograms were recorded on a Mosley Model 135 AM X-Y Recorder (18 × 25 cm). Power for the recorder and amplifiers was first fed to a Sola type CVN-1 constant-voltage transformer.

The usual sensitivity of the ΔT axis was 2·5 μV/cm (3·5° full scale), and that of the T axis was 20 μV/cm (12·5° full scale). Any 12·5° range could be selected by varying the output of the bucking source.

For the differential experiments against pure benzophenone, matching of thermal characteristics of the sample and reference cells was extremely important. Cells were constructed from 8 mm lengths of 6 mm diameter spectroscopic graphite electrodes, a lathe being used to drill holes in them 5 mm in diameter and 7 mm deep. Between runs, the cells were leached in boiling acetone for 10 min and then dried in a vacuum oven at 140° for 30 min.

Reagents

Carborundum (500-mesh) from the Carborundum Company was used as the diluent, and was prepared according to Barrall and Rogers.[4] No attempt was made to size the material except that, during the washing steps, the fines, which were slower to settle, were decanted with the wash liquid.

Reagent grade benzophenone, obtained from Columbia Organic Chemicals Company, Inc., was recrystallized three times from ligroin which had been distilled from calcium hydride. This material (designated *3RR*) was used as the reference for "active reference" runs. It was assumed to be pure within the sensitivity of this work. Eastman White Label 4-methylbenzophenone, recrystallized once from ligroin, was used as the impurity for the preparation of samples.

Samples were prepared by weighing out 10 g of benzophenone (*3RR*) and adding a weighed portion of 4-methylbenzophenone to provide the desired level of impurity. The mixture was melted in a vacuum oven at 50°, then removed and frozen quickly in a dry ice–acetone bath. After solidification, the samples were ground in a mortar and then in a Wiggle Bug mixer. Finally, the samples were mixed by repeated coning and quartering and stored in a desiccator in the dark until used.

Procedures

The sample was diluted by dissolving it in enough reagent grade diethyl ether to make a thick slurry with the carborundum, ground in a mullite mortar until the ether had evaporated, and then dried in a vacuum oven at 40°. To establish that no segregation of the impurity had occurred, a few samples were prepared by grinding the carborundum with the dry sample. An F test on the variances of the melting points of samples prepared by the two methods showed no significant difference.

The amount of thermally active material in a sample was checked by ignition in a muffle furnace.

Porcelain combustion boats were filled with the same weight of sample used in a DTA run. Weight loss was calculated after ignition to constant weight.

All runs were performed in the following manner: a pair of clean graphite cells (matched to within 1% by weight) were weighed, then filled with 0·1200 ± 0·0005 g of sample. The cells were tapped 25 times on the desk top to ensure even packing before being placed in the furnace. Thermocouples were cleaned between runs by rinsing three times with acetone and burning it off. The cell compartments were then sealed, a Dewar flask was placed round the block, glass wool was wrapped around the leads, and the programmer was started. The temperature amplifier was set in the "linear" mode to display the temperature signal on the meter of the amplifier. When the output from the pair of temperature thermocouples equalled the potential set on the bucking source, the amplifier was switched to the "recorder" mode, and the recorder itself was turned on.

This procedure was followed for both the "regular" DTA runs against the inert reference, carborundum, and the "active reference" runs against *3RR* benzophenone on carborundum. Three samples of each composition were run in triplicate so that a total of nine measurements was made for each procedure.

In the regular method, the melting point was measured at the intersection of the extensions of the baseline and the steepest part of the descending edge of the endotherm,[8] the appropriate thermocouple arrangement being used.

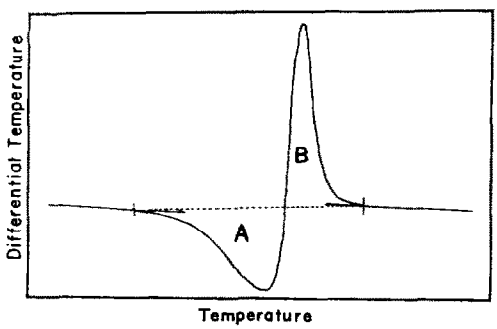

FIG. 1.—Differential thermogram obtained when a sample containing 1·01% of 4-methylbenzophenone was run against *3RR* benzophenone.

The other thermocouple arrangement was employed in the active reference method, for which a typical curve is shown in Fig. 1. For measurement of the total area, a line (shown as a dashed line in the figure) was drawn between the point of first deviation from baseline and the point of return to baseline. A polar planimeter was used to measure the area enclosed by the dashed line and the part of the curve that fell below it (Area A). A corresponding measurement was made for area B and the two areas were summed. (An attempt to use only the area of the lower portion of the curve for calibration proved impractical. A small error in establishing the baseline caused a large error in one direction. Use of the areas of both the upper and lower portions largely cancelled the errors.) The total area of a single thermogram could be reproduced with a relative standard deviation of 1%. Areas for curves resulting from repeated runs of a single portion of a sample had a relative standard deviation of 5%; areas of curves for different portions of the same sample had a relative standard deviation of 8%.

In order to estimate the area generated by mismatch of the sample and the reference cells or of the respective thermocouples, a blank was run with equal weights of *3 RR* benzophenone on carborundum in both cells. The areas under these curves were large for the first run, but for subsequent runs decreased to less than the difference in area for replicates of the differential run. The first run of either a blank or a sample gave a much larger area than later runs did. Since the thermocouples measured the temperature at a *point* in the sample, settling of the sample would have a pronounced effect on the differential signal. As a result, the first run was always disregarded and the next three used.

DISCUSSION

Melting-point depression measurements

The experimental values in the second column of Table I illustrate the capability of the instrument for determining melting points. If twice the standard deviation of the melting-point measurement was arbitrarily taken as the limit of detection, differences of less than 0·42 mole %impurity could not be detected. Comparison of

experimental melting points with theoretical melting points, calculated by the classical melting-point depression formula[7] and listed in columns three and four, indicates that the method would be useful in its present form for many of the melting-point determinations that are made. If the temperature range displayed on the recorder could have been reduced by increasing the amplification of the temperature signal, the precision of the measurements could, in principle, have been improved. However, surges in the temperature signal as the programmer cycle switched on and off were already detectable so that further expansion of the temperature axis was not feasible. Another major contribution to the uncertainty in the melting-point measurements was the spread of the endotherm due to the presence of the diluent. Use of small, pure (undiluted) samples in an instrument having a continuous programmer such as the one recently described by Barrall *et al.*[5] should make better measurements possible and, thereby, make the approach more attractive.

Active reference procedure

This procedure was carried out in two different ways. In one, the amount of active material mixed with the carborundum was adjusted, by trial and error, for the reference and each of the samples until 1g of each mixture gave very nearly the same endothermal area when measured against pure carborundum. This was done so as to match very closely the thermal behaviour of the samples. In the other, a 1-g sample of each mixture was made up to contain very nearly the same proportion by weight of active material. The latter approach was obviously faster and easier to apply.

Columns five to seven of Table I show results obtained by the first method of preparation of carborundum mixtures for analysis; columns eight and nine show results obtained by use of the second method. In both cases, samples were run against an appropriate reference of *3RR* benzophenone. For both, a straight line could be drawn through the points. For the first set, the slope of the line, as determined by regression analysis, was 2·31 in^2/mole % of impurity, and the intercept was −0·17. The standard deviation calculated by the method of least squares was 0·26. A second calibration curve prepared from a new set of samples had a slope of 2·28 in^2/mole % of impurity. The limit of detection, taken as twice the standard deviation was 0·28 mole %. The upper limit was not established experimentally, but was indicated in preliminary experiments by a decrease in slope that became a plateau when there was no overlap of the two endotherms. It should be possible to expand the range of the method by using a reference of known impurity content.

When the second method was used, the slope obtained for the least-squares line was 2·57 in^2/mole % of impurity, with an intercept of −0·20. When the slope was calculated for the same sensitivity as that used for the other procedure, the value obtained was 5·31 in^2/mole % of impurity. The relative standard deviation of an area measurement (8 % for triplicate samples) was the same as that obtained with area matching. However, the procedure was more direct in that it avoided the secondary dilutions required for area matching and, therefore, saved time. It should be noted that, in preparing the samples, a surprisingly consistent loss of 2 % of active material was observed as a result of homogenizing the samples by grinding. For example, although 0·7660 ± 0·0005 g of active material was added to 12·000 ± 0·001 g of carborundum, ignition analyses on 5-g portions generally showed 5·89 ± 0·05 % active material present. Finally, it should be noted that the slightly greater areas

TABLE I.—COMPARISON OF MELTING-POINT DEPRESSION AND ACTIVE REFERENCE METHODS FOR 0·120-g SAMPLES

Sample composition,* *mole %*	Melting point,† °C	M.p. depression, °C		Area-matched samples			Weight-matched samples	
		Calc.	Exp.	Area *vs.* carborundum,¶ $in^2/0{\cdot}120\,g$	Active material on carborundum, %	Area,** $in.^2$	Loading, %	Area, $in.^2$
0·00	$48{\cdot}7_5 \pm 0{\cdot}1$	0·00	0·00	$4{\cdot}25 \pm 0{\cdot}17$‡	$3{\cdot}6_1 \pm 0{\cdot}01$‡	$-0{\cdot}03$†† $\pm 0{\cdot}20$‡	5·79	0·00
0·282	$48{\cdot}6_3 \pm 0{\cdot}1$	0·14	$0{\cdot}1_3$	$4{\cdot}52 \pm 0{\cdot}38$	$3{\cdot}8_9 \pm 0{\cdot}08$	$0{\cdot}36 \pm 0{\cdot}36$	—	—
0·545	$48{\cdot}5_6 \pm 0{\cdot}1$	0·26	$0{\cdot}2_0$	$4{\cdot}27 \pm 0{\cdot}36$	$3{\cdot}7_2 \pm 0{\cdot}02$	$1{\cdot}18 \pm 0{\cdot}17$	5·88	$1{\cdot}19 \pm 0{\cdot}18$‡
1·01	$48{\cdot}3_2 \pm 0{\cdot}1$	0·49	$0{\cdot}4_2$	$4{\cdot}34 \pm 0{\cdot}35$	$3{\cdot}9_5 \pm 0{\cdot}04$	$1{\cdot}97 \pm 0{\cdot}21$	5·89	$2{\cdot}48 \pm 0{\cdot}31$
1·67	$48{\cdot}0_1 \pm 0{\cdot}1$	0·82	$0{\cdot}7_4$	$4{\cdot}28 \pm 0{\cdot}23$	$4{\cdot}0_3 \pm 0{\cdot}13$	$3{\cdot}72 \pm 0{\cdot}18$	5·89	$3{\cdot}65 \pm 0{\cdot}31$
1·98	$47{\cdot}8_2 \pm 0{\cdot}1$	0·97	$0{\cdot}9_2$	$4{\cdot}46 \pm 0{\cdot}28$	$4{\cdot}0_9 \pm 0{\cdot}18$	$4{\cdot}46 \pm 0{\cdot}29$	5·90	$5{\cdot}15 \pm 0{\cdot}55$

* 4-Methylbenzophenone added to *3RR* benzophenone.
† Literature value[10] $48{\cdot}25 \pm 0{\cdot}25$°C.
‡ Standard deviation.
¶ Experimental mean of all areas was $4{\cdot}35 \pm 0{\cdot}10$ $in^2/0{\cdot}120g$.
** Measured *vs.* 0·120 g of *3RR* benzophenone on carborundum.
†† The negative sign indicates that the deflections occurred in reverse order.

(for a 0·120-g sample) obtained by the weight-matched procedure were the result of using a heavier loading than in the area-matched runs.

The active reference procedure had two limitations. First, the desirability of matching the thermal properties of the samples rather closely required the use of relatively high dilutions and correspondingly high amplifications, with some sacrifice of precision. Second, the on-off cycling of the programmer produced small deviations from linearity in heating rate, to which the active reference method was extremely sensitive, particularly at high amplification. New calorimetric DTA apparatus[8] using a proportional programmer, described since this work was started, would minimize that limitation and permit the use of undiluted samples, thereby increasing the sensitivity further. The convenience and speed of this method would also be improved.

The precision of the active reference method, $\pm 0{\cdot}28$ mole %, was significantly better (at the 95% confidence level) than the 0·42 mole % of the melting point-depression procedure, as each was performed in this study. It should be noted, however, that the methods were studied under nearly identical conditions which were farthest from optimum for the melting-point depression method. However, even under these conditions, the melting-point measurements with a precision of $\pm 0{\cdot}1°$ compared very favourably with classical capillary melting-point measurements which, without special precautions, have a precision of about $\pm 0{\cdot}5°$.[9] The active reference method eliminates the need for precise temperature calibration, but the greater care required in weighing out a fixed amount of active material for dilution with carborundum offsets that advantage to some extent.

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Zusammenfassung—Die Messung der Schmelzpunktsdepression unreiner Proben wurde mit einer Differenzmethode verglichen, bei der die unreine Probe gegen eine reine Probe desselben Materials gemessen wurde. Es wurden Proben aus hoch gereinigtem Benzophenon untersucht, denen bekannte Mengen 4-Methylbenzophenon zugesetzt waren. Die Fläche unter der Kurve war proportional der Reinheitsdifferenz zwischen Probe und Bezugsmaterial im Bereich von 0,3 bis 2,0 Mol-% mit einer Standardabweichung von 0,10 Mol-%. Diese Unsicherheit ist nur halb so groß wie die bei der Schmelzpunktsdepressionsmethode mit derselben Apparatur.

Résumé—La mesure de la dépression du point de fusion d'échantillons impurs a été comparée à une méthode différentielle comprenant le traitement de l'échantillon impur parallèlement à un échantillon pur du même produit. On a étudié des échantillons de benzophénone hautement purifiée à laquelle on a ajouté des quantités connues de 4-méthylbenzophénone. L'aire de la courbe est proportionnelle à la différence de pureté entre l'échantillon et la substance de référence dans le domaine étudié, 0,3–2,0 moles % avec un écart type de 0,10 mole %, une incertitude qui n'est que la moitié de celle obtenue par la méthode de dépression du point de fusion avec le même appareil.

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ANALYTICAL CHEMISTRY OF CYCLAMATES: A REVIEW

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Summary—The analytical chemistry of cyclamates is reviewed, the emphasis being on methods of assay, tests for impurities and methods of determination in food and drug products.

INTRODUCTION

ALTHOUGH a variety of chemicals other than carbohydrates have a sweet taste, only two synthetic sweetening agents are safe for use in beverages, drugs and food; cyclamates and saccharin.

Saccharin, discovered in 1879, has been commercially available since 1900. Its properties and those of the various saccharin salts and derivatives have been reviewed.[1,2]

Cyclamate, discovered in 1937, became available in 1950. Since then several articles describing the use[3,4] and properties[5] of cyclamate have been published. Cyclamate is the generic name for cyclohexylsulphamates. The sodium and calcium salts and the free acids are commercially available.

This paper reviews the methods which are used for the analysis of cyclamates and include methods of assaying, tests for impurities and the determination of cyclamate in food and drug preparations.

METHODS OF ASSAY

One of the earliest official methods of assaying cyclamate materials is given in the United States Pharmacopoeia;[6] the nitrogen content of calcium cyclamate is determined by Kjeldahl's method.

The National Formulary XI[7] recommends the assay of sodium cyclamate by treatment of an acidified solution of sodium cyclamate with an excess of nitrous acid in the presence of excess of barium chloride and then the weighing of the precipitated barium sulphate.

The First Addendum to the British Pharmacopoeia 1963[8] describes a variety of procedures for the assay of cyclamate materials. In calcium cyclamate, the calcium is determined by titration with EDTA and the cyclamate by a nitrogen determination similar to that described above.[6] Cyclamic acid is determined by titration with standard alkali, and the sodium salt by non-aqueous titration (acetic/perchloric acid) of the cation.

Perhaps the best procedure for the assay of cyclamate is that described in the National Formulary XII.[9] The calcium and sodium salts are titrated with nitrous acid, either a starch/iodide external indicator being used or an electrometric detection of the end-point similar to that described in the General Procedures of the British Pharmacopoeia 1963.[10] In the writer's opinion the best method for the assay of

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cyclamate materials is that based on the titration with nitrous acid, as this is the only procedure which directly determines the active grouping (—$NHSO_3^-$).

TESTS FOR IMPURITIES

Acidity or alkalinity[8]

The B.P. 1963 Addendum 1964 describes a simple pH determination in a 10% w/v aqueous solution of the calcium or sodium salt.

Sulphate[8]

This is carried out by the usual turbidimetric procedure.

Water[8]

In the case of the calcium salt dihydrate, the water is best determined by the Karl Fischer method. For the sodium salt and the free acid, oven-drying at 105° is quite adequate.

Sulphated ash (cyclamic acid only)[8]

This is determined in the conventional manner by ashing in the presence of sulphuric acid in a platinum dish.

Heavy metals[6,9]

These are determined by the United States Official methods, *i.e.*, by reaction with sulphide under mildly acidic conditions.

Cyclohexylamine

The Ministry of Health Statutory Instruments,[11] describe an inadequate test based on the reaction of cyclohexylamine, or other amine present, with an excess of sodium carbonate in warm water to produce ammonia. The test states that "no distinct odour of ammonia" should be observed. We have found this test to be sensitive only to about 1200 ppm of cyclohexylamine.

For the sodium salt and cyclamic acid we have devised a simple test based on the reaction of Nessler's reagent with the amine to give a white precipitate, which can be estimated turbidimetrically. This procedure is sensitive to about 500 ppm of cyclohexylamine.

We have also confirmed Morris's[12] findings that the cyclohexylamine can be extracted from an alkaline solution of the cyclamate material with benzene; the resulting benzene solution, after acidification, reacts with picryl chloride to form an intensely yellow coloured picrylamine which can be measured spectrophotometrically (λ_{max} 418 mμ). This procedure, which offers the most sensitive procedure for cyclohexylamine in cyclamate materials, is sensitive to 50 ppm of cyclohexylamine, but is relatively lengthy.

DETERMINATION OF CYCLAMATES IN FOOD AND DRUGS

Ion-exchange procedures

Komoda and Takeshita,[13] have separated saccharin, cyclamic acid and dulcin from food by adsorption onto Amberlite CG400 Type 1, Cl form. The cyclamic acid and the saccharin are then eluted with oxalic acid and alcohol. The eluate is neutralized and examined by paper chromatography, as described below.

Asano *et al.*[14] have used a similar system. They used Amberlite CG46 (Cl form)

for the sorption, and eluted cyclamic acid with 0·1*M* hydrochloric acid. They then titrated the cyclamic acid with nitrous acid and determined the sulphate nephelometrically.

These methods are rather lengthy and in many cases can be superseded by the titrimetric, gravimetric, spectrophotometric and gas chromatographic techniques described below, especially the first.

Yamaguchi[15] has described a useful procedure for the separation of sulphamic and cyclamic acids on Amberlite IRA-400 and IR46, with methanol and 0·05*M* hydrochloric acid as eluting agents.

Paper and thin-layer chromatography

Mitchell has proposed a method based on paper chromatography.[16] Cyclamic acid, saccharin and dulcin in foodstuffs are extracted with ethyl acetate after acidification with sulphuric acid. The solvent is evaporated off and the residue dissolved in ammoniacal 50% aqueous ethanol is applied to the paper. Separation is completed by ascending chromatography with a mobile phase of acetone–ethyl acetate–ammonia (8:1:1). Cyclamic acid and saccharin give white spots when sprayed first with 0·005*M* silver nitrate in ammoniacal ethanol and then with 0·0005*M* pyrogallol in ethanol. We have used this system for thin-layer chromatography on cellulose and found it to be satisfactory.

Ko *et al.*[17] separated the sweetening agents by paper chromatography with a mobile phase of n-butanol–10% ammonia (4:1) and a spray reagent consisting of a dilute nitric acid solution containing pyrogallol and silver nitrate for the detection of cyclamic acid. Komada and Takeshita[13] used a similar procedure, but favoured a mobile phase of isoamyl alcohol–pyridine–water, which gave less interference from food preservatives such as salicyclic, benzoic and sorbic acids.

Salo *et al.*[18] and Salo and Salminen[19] favour a stationary phase of 10% acetylated cellulose containing 40% of polyamide for thin-layer chromatography. They use Shell Sol A (an isomeric mixture of methyl benzenes)–isopropanol–glacial acetic acid–formic acid (45:6:7:2) as the mobile phase, and locate the sweetening agents with Rhodamine B. We have successfully used this procedure with Rhodamine B as internal locating agent.

Ichibagase and Kojima[20] recommend mobile phases of ethyl acetate–glacial acetic acid–water (4:1:2) or ethyl acetate–formic acid–water (4:1:2) or ethyl acetate–ethanol–glacial acetic acid–water (4:2:1:2). For location they hydrolyse cyclamic acid to cyclohexylamine with hydrogen peroxide and finally spray with quinhydrone to give a violet spot.

Kamp[21] used silica gel G thin-layer plates and a mobile phase of either acetone–10% ammonia (90:10) or acetone–10% ammonia–ethyl acetate (80:10:10) and subsequently sprayed these plates with Mitchell's reagent.[16]

We have examined these systems and found that Salo's[18,19] give very clean chromatograms. We have also satisfactorily used a mobile phase of n-butanol–glacial acetic acid–water (4:1:5) (upper phase only) with 0·015% w/v Bromophenol Blue as locating agent, and a mobile phase of ethanol–ammonia (s.g. 0·880)–water (20:4:1) with 0·040% w/v Bromocresol Green as locating agent, on cellulose thin-layer plates. In general we have found that locating agents containing silver

nitrate[13,16,17,21] are not completely satisfactory and it is suggested that it may be preferable to incorporate this reagent in the thin layer itself.

All these procedures have the shortcoming that if cations are present, spots will be obtained not only for cyclamic acid but also for the salt.

Titrimetric methods

Vercillo and Manzone[22] treated the salts of cyclamic acid with excess of nitrous acid and then titrated the liberated sulphate with standard barium solution, tetrahydroxyquinone being used as indicator, after removal of calcium by ion-exchange.

The National Formulary XII[9] describes a simple titrimetric procedure for the determination of the cyclamate content of compound calcium cyclamate and calcium saccharin tablets. Cyclamate is titrated in acid solution with sodium nitrite, starch-iodide being used as an external indicator.

Richardson and Luton[23] have described a similar procedure for cyclamate in comminuted and other fruit drinks, but detect the end-point electrometrically. It has proved one of the most satisfactory and simple techniques for the determination of cyclamate in food and drugs. It is usually only necessary to acidify the sample with mineral acid and titrate electrometrically with sodium nitrite solution. This method has been successfully used for the determination of cyclamate in sauces. For the determination of cyclamate in biscuits a simple water extraction, before titration, proved to be adequate. In the case of a drug preparation (an expectorant) containing a substantial quantity of a thickening agent, it was found desirable to acidify the drug preparation to pH $< 0{\cdot}6$, extract with chloroform (preferably in a continuous liquid–liquid extractor) evaporate off the chloroform, dissolve the residue containing the cyclamate in dilute mineral acid, and titrate it.

Gravimetric determination

This is the oldest method of analysis for cyclamate; it is generally reliable but is time consuming.

The United States Pharmacopoeia XVI[6] gives a gravimetric procedure for the determination of the cyclamate content of compound calcium cyclamate and calcium saccharin solution and tablets. The cyclamate is treated with an excess of nitrous acid in the presence of excess of barium chloride and the barium sulphate formed is filtered off, dried and weighed.

Wilson[24] and Cox[25] have used similar procedures for the determination of sodium cyclamate in canned fruit and similar products.

Wilson[26] has described a lengthy procedure for determining sodium cyclamate in sugar-free beverages. The beverage is first neutralized and then evaporated to dryness. The sodium salt is extracted with hot ethanol, which is then evaporated off and the residue is dissolved in water. The cations are removed by ion-exchange, and the effluent is evaporated to dryness and the residue is first extracted with chloroform, and then dried and weighed as cyclamic acid. The analysis is finally checked by the barium sulphate method. If pectin is present it is removed before the determination by alcoholic precipitation.

Knelhofer and Aumann[27] recommend a procedure for the determination of cyclamates in wine. The wine is made alkaline with sodium hydroxide and then just acidified with hydrochloric acid (Methyl Orange as indicator) and then oxidized

with hydrogen peroxide. The resulting sulphamic acid is hydrolysed to sulphate which is then precipitated, filtered off and weighed as barium sulphate.

Giodano and Pennati[28] have confirmed that cyclamate in wines can be identified by paper chromatography by Mitchell's[16] procedure, but have noted that the procedures of Wilson[24] and Cox[25] are not possible owing to interference by sulphur dioxide, which is always present in wines. They recommend removing the effect of the sulphur dioxide by first boiling the wine with hydrochloric acid, then adding excess of barium chloride, boiling again, filtering off any barium sulphate and other insoluble materials and finally treating with sodium nitrite, reheating, filtering off the precipitated barium sulphate, igniting and weighing. This procedure has the great advantage that any turbidity arising from interaction of the sodium nitrite with colouring matter, leaves no residue on ignition and hence does not interfere.

Mihashi and Kobayashi[29] have described a procedure in which the cyclamic acid is separated by solvent extraction with ether or ethyl acetate after acidification. The solvent is evaporated off and the extracted cyclamic acid is treated with hydrochloric acid and sodium nitrite. The resulting sulphate is then precipitated with an excess of standard barium chloride and the excess of barium is titrated with standard EDTA. They indicate that the method is suitable for drug preparations, carbonated beverages (not containing sulphur dioxide), *etc.* but it is not suitable for foodstuffs containing antiseptics.

Both this procedure and that of Wilson[26] suffer from the objection that unless the pH of the mixture is less than 0·6 (*q.v.* Beck[5]) then the extraction of the cyclamic acid is unlikely to be quantitative.

Infrared spectroscopy

Oba *et al.*[30] recommend infrared spectroscopy for the determination of cyclamic acid in the presence of carbohydrates, *etc.* They carried out the determination by the potassium bromide disc technique without isolation of the acid. The absorption band at 800 cm^{-1}, characteristic of cyclamic acid, was used and the measurements were made by the base-line method in order to overcome the absorption by saccharin and dulcin at this frequency. When lactose was used as the vehicle, the differential method was applied. The results gave errors of up to 10% so that, even if complex calculations involving matrix algebra were applied, it is unlikely that the method could be widely used quantitatively for the determination of cyclamate in complex mixtures in food and drug preparations.

Colorimetry

Gianferrara[31] extracted cyclamic acid from acidified beverages with petroleum ether and evaporated the extract to dryness. The extract was dissolved in propylene glycol–ethanol (6:4) solvent mixture and warmed, and a drop of hydrogen peroxide was added, followed by two drops of a 1% benzene solution of chloranil; the violet colour produced was measured spectrophotometrically; the calibration curve was linear.

Kojima and Tchibagase[32] treated sodium cyclamate with hydrochloric acid and hydrogen peroxide and allowed the solution to digest at 100° for 2 hr. Sodium hydroxide and manganese dioxide were added and the mixture was stirred, diluted with water and centrifuged. Atkins and Poutin buffer and ethanolic quinhydrone

solution were added to an aliquot of the supernatant liquid. The mixture was heated at 60° for 10 min and then allowed to cool to room temperature; a 10% solution of acetic acid in chloroform was added and the solution was thoroughly mixed. The chloroform phase was separated and its absorbance at 355 mμ was measured.

A second procedure consists of treating the cyclamic acid with hydrogen peroxide and hydrochloric acid for 1–5 hr at 100°, neutralizing the cooled mixture with sodium hydroxide, adjusting the pH to 12 and heating with quinhydrone in ethanol, extracting with chloroform and measuring the absorbance at 495 mμ.

They report that dulcin, putrifying amines and colouring materials, *etc.* interfere, but can be removed by preliminary treatment with ion-exchange resin and/or solvent extraction.

Ichikawa *et al.*[33] have hydrolysed sodium cyclamate with hydrochloric acid and hydrogen peroxide to form cyclohexylamine. When the cyclohexylamine content is less than 0·025% the amine is extracted into chloroform and treated with quinhydrone or 1,4-benzoquinone in ethanol, and kept at 50° for 2 hr to give 2-(cyclohexylamine)-1,4-benzoquinone which can be measured spectrophotometrically.

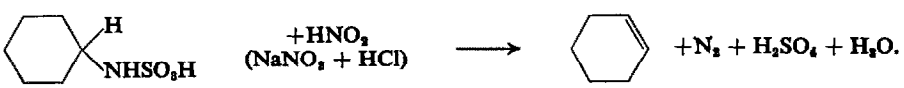
When the concentration of cyclohexylamine is greater than 0·25%, manganese dioxide is added to decompose excess of hydrogen peroxide, the pH is adjusted to 9·0, a solution of quinhydrone in ethanol is added and the mixture is kept at 50° for 15 min. It is then extracted with chloroform to give 2,5-bis(cyclohexylamine)-1,4-benzoquinone which can then be measured spectrophotometrically.

In our experience colorimetric procedures are tedious and usually do not give very accurate results, especially for the determination of cyclamate in complex food and drug products.

Gas chromatography

Rees[34] has described a gas chromatographic procedure for the determination of cyclamate in fruit drinks.

The procedure is based on the reaction with nitrite:—



The cyclohexene formed is extracted and then determined by gas chromatography on a silicone oil column. Richardson and Luton[35] have examined and modified this procedure by ensuring that the pH of extraction is in accordance with Beck's[5] recommendations and by using sulphuric acid in place of hydrochloric acid in order to avoid the formation of monochlorocyclohexane. They recommended a polyethylene glycol 400 column and found that in addition to cyclohexene they could detect the presence of substantial quantities of cyclohexanol and cyclohexanone; monochlorocyclohexane was also detected if hydrochloric acid was used.

Gas chromatography, although a reliable technique for determining cyclamate in fruit drinks is, by comparison with the simple titration procedure,[23] rather time-consuming, and requires more expensive equipment and manipulative skill.

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Résumé—On passe en revue la chimie analytique des cyclamates, en insistant sur les méthodes de détermination, les essais pour impuretés et les méthodes de dosage dans les produits alimentaires et pharmaceutiques.

Zusammenfassung—Es wird eine Übersicht über die analytische Chemie von Cyclamaten gegeben, wobei besonderes Gewicht auf die Nachweismethoden, Reinheitsprüfung und die Bestimmung in Lebensmitteln und Drogen gelegt wird.

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2-(2-THIAZOLYLAZO)-4-METHOXYPHENOL AND 2-(2-THIAZOLYLAZO)-5-METHOXYPHENOL AS METAL-ION INDICATORS

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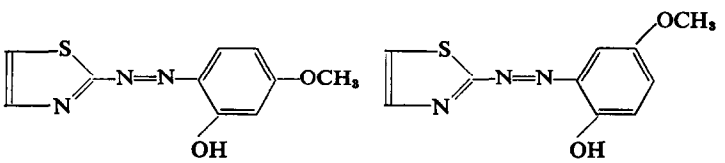
Summary—2-(2-Thiazolylazo)-5-methoxyphenol (TAMR) and 2-(2-thiazolylazo)-4-methoxyphenol (TAMH) are shown to be good indicators for the titration of many metal ions with EDTA. TAMH is better and more widely applicable than TAMR. The acid dissociation constants have been determined by spectrophotometry. The effect of pH on the absorbance of the indicators and metal-indicator complexes is reported.

2-(2-THIAZOLYLAZO)-5-METHOXYPHENOL (TAMR) and 2-(2-thiazolylazo)-4-methoxyphenol (TAMH) resemble 4-(2-thiazolylazo)resorcinol (TAR) in their properties as metal-ion indicators. TAMH, and a family of thiazolylazo dyes, has been prepared by Kawase,[1] who has also studied its complexes with some bivalent metal ions[2,3] and cobalt(III).[4] We showed that TAMH especially was more useful than TAR when used for high-precision EDTA-titrations of a number of metal ions. This study is concerned with the behaviour of these compounds as metal-ion indicators.



EXPERIMENTAL

Reagents

2-(2-Thiazolylazo)-5-methoxyphenol (TAMR) and 2-(2-thiazolylazo)-4-methoxyphenol (TAMH). Prepared by Svoboda and Bendová[15] and purchased from Lachema, Brno or Chemapol, Prague. TAMH in the form of bright dark-green crystals, and TAMR, a brown crystalline powder, are sparingly soluble in ether, dioxane and water, but very soluble in dimethylformamide, methanol, ethanol, acetone and chloroform, giving red and yellow-orange solutions respectively. Doubly recrystallized from hot ethanol, the samples contained 99–100% of active dye.

The purity of the dyes was checked by descending paper chromatography with 80% v/v aqueous ethanol as eluent, by elemental analysis, and by determination of the inorganic sulphate in the ashed material (<0·1%). Solutions, 0·1*M* or 0·1%, of TAMH and TAMR in methanol were generally used, but solutions in 0·2*M* ammonia are suitable. Traces of heavy metal ions were masked by 1 drop of 0·05*M* EDTA solution.

pH-Control. The pH was adjusted with dilute perchloric acid or sodium hydroxide for the spectrophotometric measurements. For qualitative studies the following buffer solutions were used: sodium acetate/hydrochloric acid (pH 2–5), hexamethylenetetramine/nitric acid (pH 5–6·5) or tris(hydroxymethyl)aminomethane/hydrochloric acid (pH 7–9).

For EDTA-titrations, hexamethylenetetramine buffer (0·1*M* with respect to base) of pH 6 and acetate buffer (0·79*M* with respect to base trihydrate) of pH 4·5.

Acidities below pH 1 were calculated from the perchloric acid concentrations corrected by the appropriate activity coefficients,[6] or were expressed by the H_0 function.[7,8]

Ionic strength. For spectrophotometric studies an ionic strength of 0·1 was maintained with sodium perchlorate.

Metal nitrate solutions. Standardized chelometrically by obvious procedures. All chemicals were of analytical grade.

EDTA, 0·025M and 0·05M solutions. Standardized by lead chloride with Xylenol Orange as indicator.[9]

Apparatus

A CF-4 spectrophotometer (Optica, Milano) with 10-mm and 50-mm silica cells. Radiometer PHM 28 pH meter.

RESULTS AND DISCUSSION

Acid-base equilibria of TAMH and TAMR

Three optically different forms exist in solution, depending on the pH. For TAMH the solutions are orange-red at pH < 1, yellow at pH 1–7 and violet at pH 7·5–8, the colours being due to the forms H_2R^+, HR and R^- respectively. For TAMR the corresponding forms are red at pH < 2, yellow at pH 2–5·5 and red at pH > 5·5. The spectra show isosbestic points corresponding to these transitions (Figs. 1 and 2).

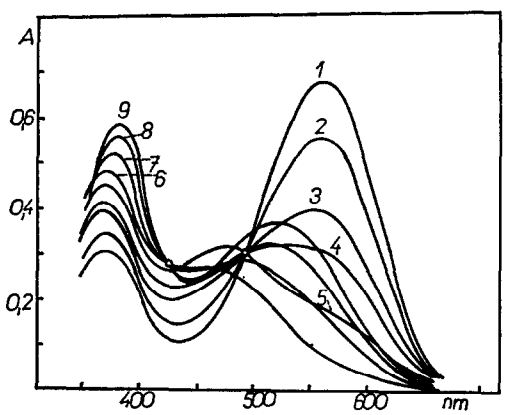


FIG. 1.—Dependence of absorption spectra of TAMH on pH.

$C_R = 5·0 \times 10^{-5}M$, in 0·5% v/v methanol.
pH: *1*—10·80; *2*—8·10; *3*—8·11; *4*—7·59; *5*—7·35; *6*—0·81; *7*—0·42; *8*—0·14; *9*—H_0 = −0·33.

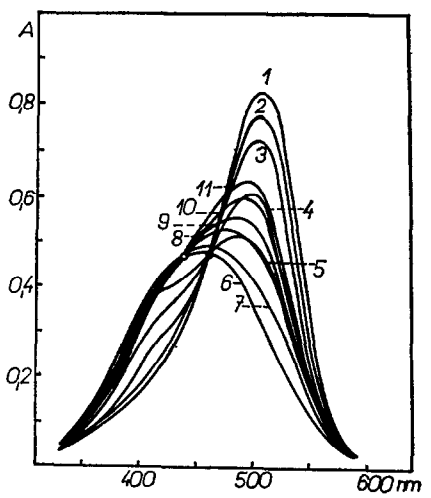


FIG. 2.—Dependence of absorption spectra of TAMR on pH.

$C_R = 3 \times 10^{-5}M$, in 0·5% v/v methanol.
pH: *1*—10·80; *2*—8·50; *3*—8·05; *4*—7·31; *5*—6·83; *6*—1·42; *7*—1·01; *8*—0·81; *9*—0·64; *10*—0·42; *11*—0·14.

The molar absorptivities for the various forms were calculated from the horizontal lines of pH–absorbance plots and graphically from plots of $C_R/A = f\{[H]\}$ and from equations (1) and (2),[10] or the logarithmic form [equation (3)],[11] which were used to calculate the dissociation constants. The calculations were made from the absorbances at 510 and 550 mμ for TAMH and 410 and 500 mμ for TAMR.

If the acid dissociation constants are given by

$$K_{a1} = \frac{[HR][H^+]}{[H_2R]} \text{ and } K_{a2} = \frac{[R^-][H^+]}{[HR]},$$

then for the second step only:

$$\frac{C_R}{A} = \frac{1}{\varepsilon_R} + \frac{[H](A - \varepsilon_{HR}C_R)}{A\varepsilon_R K_{a_2}} \quad (1)$$

$$\frac{C_R}{A} = \frac{1}{\varepsilon_{RH}} + \frac{(A - \varepsilon_R C_R)K_{a_2}}{A[H]\varepsilon_{RH}} \quad (2)$$

$$\log \frac{A - \varepsilon_{HR}C_R}{\varepsilon_R C_R - A} = \text{pH} + \log K_{a_2} \quad (3)$$

where A is the total absorbance, C_R the analytical concentration of indicator and ε_x is the molar absorptivity of species x. The constants determined for both indicators are shown in Table I.

TABLE I.—SUMMARY OF OPTICAL AND ACID DISSOCIATION CONSTANTS FOR TAMH AND TAMR

	TAMH			TAMR	
	λ_{max}		$\varepsilon \times 10^{-4}$	λ_{max}	$\varepsilon \times 10^{-4}$
H_2R^+	380,	523	1·36	491	2·70
HR	370,	468	0·78	418	1·67
R^-	370,	561	1·38	505	2·74
pK_{a1}		$-0·3 \pm 0·03$*			$0·98 \pm 0·02$*
isosbestic points, mμ		423			439
pK_{a2}		$8·13 \pm 0·02$†‡§			$6·70 \pm 0·04$†‡
isosbestic points, mμ		493			462

* Average of 2 values † Average of 4 values ‡ $\mu = 0·1$
§ 8·4 in 20% v/v dioxane[1]

The yellow form is the most suitable for titrations so the useful pH ranges for TAMH and TAMR are 1·5–6 and 2·0–5 respectively (Figs. 3 and 4). They have the advantage of a simple dissociation scheme compared to TAR. However, the reactions with ions at pH > 7 are often difficult to observe owing to the considerable increase in absorbance of the indicator anion; horizontal parts of the pH–absorbance plots, which indicate quantitative formation of a particular metal complex, are sometimes obtained with difficulty.

Analytical reactions of TAMH and TAMR

TAMH reacts with a number of metal ions giving green, blue-green or blue complexes (Fig. 5); TAMR forms red or red-orange ones under similar conditions (Fig. 6). They can usually be destroyed by EDTA and are extractable into polar solvents such as isoamylol or ethyl acetate. There is little difference in the analytical behaviour of the reagents, although with TAMH the colour change in the presence of metal ions is slightly better; both, but especially TAMR, resemble TAR.

When $C_R = C_M = 10^{-3}$–$10^{-4}M$ the following ions react with TAMH and TAMR:
pH < 2·5; Cu(II), Zr(IV), Bi(III), UO_2(VI), Pd(II), Tl(III), Hg(II), Ti(IV), V(V), V(IV), Nb(V) in the presence of tartrate, Ta(V) in the presence of oxalate;
pH 2·5–6; Zn(II), Cd(II), Hg(II), Sc(III), In(III), Ga(III), Y(III), La(III), lanthanides, Th(IV), Ti(IV), Fe(III), Ni(II), Co(II), Pb(II), Ta(V) in the presence of oxalate;
pH 6–9; Ca(II), Al(III), Sn(IV), Cr(III) (all after boiling), Mo(VI), W(VI), Sb(III), Mn(III).

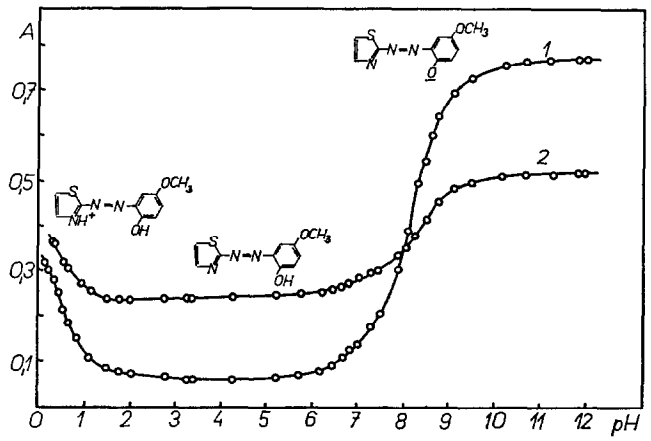


FIG. 3.—pH-Absorbance plots of TAMH.
$C_R = 5 \times 10^{-5} M$, in 0·5% v/v methanol;
1—550 mμ; *2*—510 mμ.

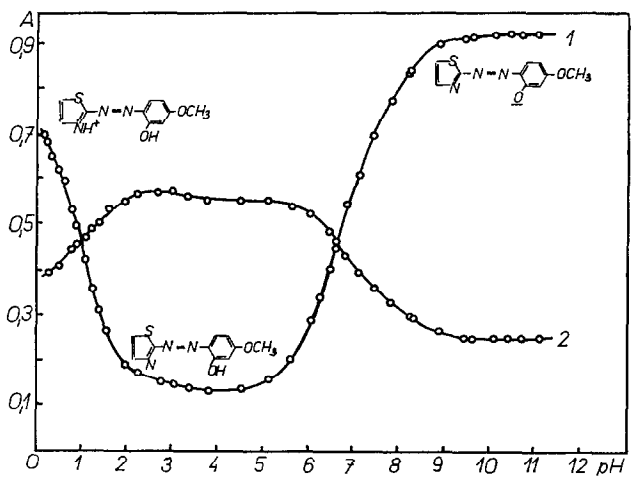


FIG. 4.—pH-Absorbance plots of TAMR.
$C_R = 3 \times 10^{-5} M$, in 0·5% v/v methanol.
1—500 mμ; *2*—410 mμ.

However, Mg(II), Sr(II), Ba(II), Al(III), Sn(IV), As(III), Sb(III), Cr(III), Mo(VI), W(VI), Se(IV), Te(IV) and platinum metals with the exception of Pd(II), do not give distinct colour changes. Cerium(IV) oxidizes the indicators and Sn(II) and Ti(III) reduce them.

It is evident that the sensitivity of the reactions strongly depends on pH. The maximal sensitivity and the corresponding pH values for reactions with several ions are given in Table II.

Metal complexes formation with TAMH and TAMR

pH-Absorbance plots at selected wavelengths, and absorption curves for equimolar solutions or for solutions containing excess of metal ion ($C_M/C_R \sim 50$) give

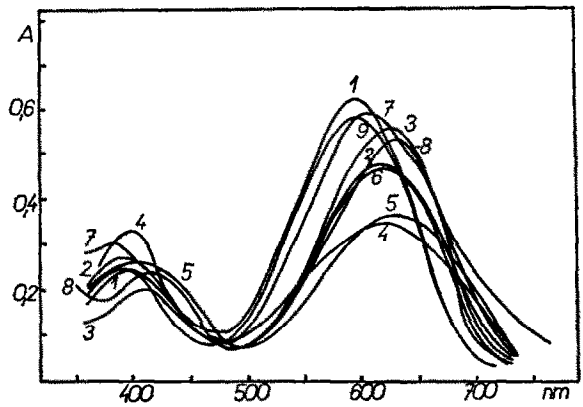


FIG. 5.—Absorption spectra of TAMH chelates with various metal ions.
$C_R = 4 \times 10^{-5}M$, $C_M = 2 \times 10^{-3}M$.
1—Zn(II), pH 7·60; *2*—Pb(II), pH 5·81; *3*—Hg(II), pH 6·0;
4—Co(II), pH 6·72; *5*—Bi(III), pH 2·20; *6*—In(III), pH 3·58
7—Ni(II), pH 7·10; *8*—Cu(II), pH 6·20; *9*—Cd(II), pH 7·70.

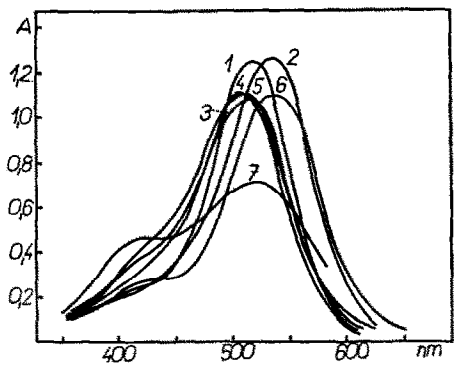


FIG. 6.—Absorption spectra of TAMR chelates with various metal ions.
$C_R = 4 \times 10^{-5}M$, $C_M = 2 \times 10^{-3}M$.
1—Ni(II), pH 7·45; *2*—Cu(II), pH 6·20; *3*—Zn(II), pH 7·40;
4—Cd(II), pH 7·70; *5*—Co(II), pH 8·11; *6*—Hg(II), pH 6·38;
7—Pb(II), pH 6·52.

evidence of the formation of 1:1 complexes with TAMH and TAMR. If the concentrations of metal ion and reagent are fixed the complexes with TAMH are formed at lower pH than those with TAMR (Figs. 7 and 8). Typical absorption curves for some metal complexes with TAMH and TAMR have already been shown in Figs. 5 and 6. The complexation equilibrium:

$$M^{n+} + HR \rightleftharpoons MR^{(n-1)+} + H^+$$

in solutions containing excess of metal ion can be characterized by pH-dependent absorption curves; to conserve space, only those for the systems of copper(II)-TAMH and copper(II)-TAMR are shown (Figs. 9 and 10). In general, sharp isosbestic points are found. The diffuse inflexion at 420 mμ in the TAMR system is similar to those of the MRH complexes of TAR and 4-(2-pyridylazo)resorcinol (PAR). A

TABLE II.—MAXIMAL SENSITIVITY OF SOME REACTIONS OF TAMH AND TAMR WITH METAL IONS

	TAMH		TAMR	
	pD*	pH	pD*	pH
Cu(II)	6·7	4·5–7·0	6·7	6·0
Zn(II)	7·0	7·0	7·3	7·0
Cd(II)	6·6	6·0	5·8	7·0
Pd(II)	5·9	6·0	5·6	6·0
Ni(II)	7·0	6·0	7·0	7·0
Co(II)	6·7	6·0	6·7	7·0
Hg(II)	6·2	6·0	6·6	6·0
Bi(III)	6·2	3·0	5·8	3·0
In(III)	5·6	4·5	5·8	5·3
Ga(III)	5·4	5·3	6·1	5·3
Tl(III)	6·0	5·3	5·7	5·3
Lanthanides	6·1–6·5	7–8	5·8–5·9	7–8

* Sensitivity values correspond to 1 ml of solution containing 1 drop of $10^{-3}M$ reagent and 0·8 ml of suitable buffer solution; pD = −log (dilution limit).

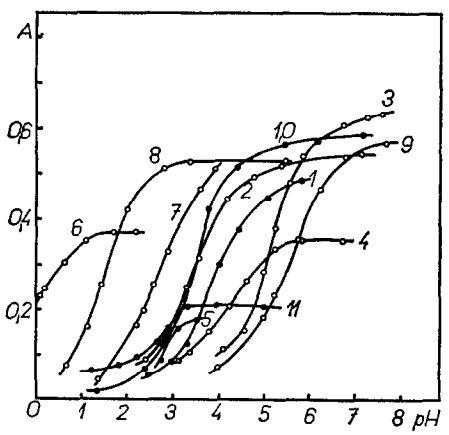


FIG. 7.—pH-Absorbance plots of TAMH solutions in the presence of excess of metal ion.

$C_R = 4 \times 10^{-5}M$, $C_M = 2 \times 10^{-3}M$:
1—Pb(II), 618 mμ; *2*—Hg(II), 628 mμ; *3*—Zn(II), 594 mμ;
4—Co(II), 518 mμ; *5*—Ga(III), 613 mμ; *6*—Bi(III), 632 mμ;
7—In(III), 618 mμ; *8*—Cu(II), 631 mμ; *9*—Cd(II), 598 mμ;
10—Ni(II), 608 mμ; *11*—Tl(III), 626 mμ; $C_R = C_M = 4 \times 10^{-5}M$.

large absorbance due to the ligand, at 425–430 mμ, was only found for the lead(II)–TAMR system at pH 6·52, where formation of the ligand anion and hydrolysis of lead(II) are significant. No sharp isosbestic point was found for this system.

The part of the spectrum of the TAMH complexes below 500 mμ shows the strong influence of the cationic field on the dye spectrum. Optical data for some metal complexes of TAMH and TAMR are shown in Table III.

The difference in λ_{max} between the HR-form of the indicator and its metal complex is greater for TAMH (126–164 mμ) than for TAMR (90–120 mμ). The shift is large enough for both to function as metal-ion indicators.

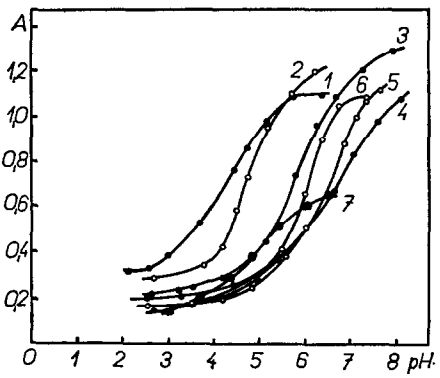


FIG. 8.—pH-Absorbance plots of TAMR solutions in the presence of excess of metal ion.
$C_R = 4 \times 10^{-5} M$, $C_M = 2 \times 10^{-3} M$:
1—Hg(II), 537 mμ; *2*—Cu(II), 535 mμ; *3*—Ni(II), 520 mμ;
4—Co(II), 511 mμ; *5*—Cd(II), 508 mμ; *6*—Zn(II), 513 mμ;
7—Pb(II), 538 mμ.

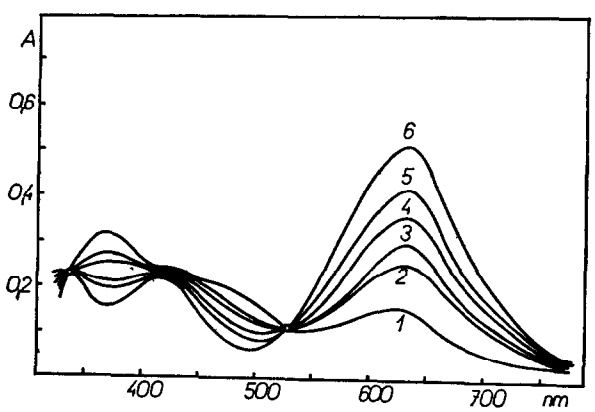


FIG. 9.—Dependence of absorption spectra of copper(II)–TAMH complex on pH.
$C_R = 4 \times 10^{-5} M$, $C_M = 3 \times 10^{-3} M$.
pH: *1*—1·10; *2*—1·40; *3*—1·72; *4*—2·0; *5*—2·50;
6—6·20.

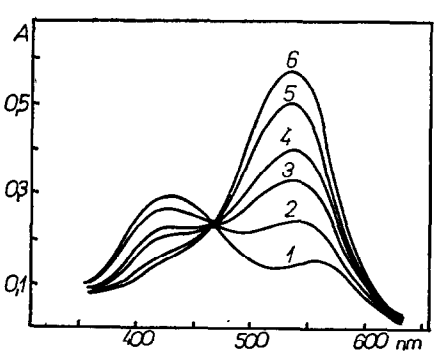


FIG. 10.—Dependence of absorption spectra of copper(II)–TAMR complex on pH.
$C_R = 2 \times 10^{-5} M$, $C_M = 1 \times 10 - 3M$.
pH: *1*—2·70; *2*—4·40; *3*—4·98; *4*—5·16; *5*—5·50;
6—6·12.

TABLE III.—OPTICAL DATA FOR SOME 1:1-COMPLEXES OF TAMH AND TAMR

	TAMH		TAMR	
	λ_{max}, $m\mu$	$\varepsilon \times 10^{-4}$	λ_{max}, $m\mu$	$\varepsilon \times 10^{-4}$
Cu(II)	631	1·34	535	3·08
Cd(II)	598	1·46	508	2·78
Pb(II)	618	1·20	520	—
Hg(II)	628	1·40	537	2·75
Zn(II)	594	1·56	513	2·70
Bi(III)	632	0·92	542*	—
Tl(III)	626*	—	529*	—
Ni(II)	608	1·50	520	3·10
Co(II)	618	0·87	511	2·75
In(III)	618	1·18	—	—

* Curves taken for equimolar solutions with $C = 4 \times 10^{-5} M$.

TABLE IV.—THE PRECISION OF EDTA TITRATIONS OF SOME METAL IONS WHEN TAMH AND TAMR ARE USED AS INDICATORS

		TAMH		TAMR	
Ion	Taken, *mg*	Found, *mg*	Confidence interval, *mg*	Found, *mg*	Confidence interval, *mg*
Cu(II)	3·18	3·18	±0·015	3·18	±0·021
	15·92	15·92	0·005	15·91	0·021
	31·83	31·82	0·025	31·83	0·025
Pb(II)	10.20	10·19	±0·051	10·19	±0·051
	30·62	30·62	0·051	30·62	0·051
	61·20	61·18	0·051	61·18	0·051
Cd(II)	5·65	5·61	±0·050	5·66	±0·050
	16·94	16·91	0·060	16·96	0·060
	33·89	33·88	0·060	33·91	0·065
Zn(II)	3·33	3·30	±0·015	3·32	±0·025
	16·66	16·64	0·041	16·62	0·031
	33·32	33·29	0·015	33·30	0·015
Hg(II)	5·01	5·03	±0·020	5·03	±0·031
	10·01	10·02	0·005	10·03	0·025
	25·04	25·06	0·020	25·07	0·025
Co(II)	2·85	2·84	±0·010	2·88	±0·023
	14·23	14·22	0·031	14·22	0·046
	28·45	28·46	0·023	28·45	0·023
Ni(II)	2·97	2·98	±0·015	2·98	±0·015
	14·86	14·87	0·015	14·86	0·015
	29·70	29·67	0·031	29·68	0·041
Bi(II)	10·47	10·49	±0·050	10·49	±0·050
	31·40	31·40	0·050	31·41	0·050
	62·80	62·78	0·050	62·84	0·050
Ti(III)	33·78	33·77	±0·050	33·80	±0·045
	67·58	67·62	0·030	67·68	0·055
	135·16	135·20	0·150	135·30	0·150
In(III)	5·76	5·71	±0·060		
	17·29	17·30	0·035		
	34·59	34·60	0·031		

TAMH and TAMR as metal-ion indicators in EDTA-titrations

Both indicators are suitable for the EDTA-titration of Cu(II), In(III), Bi(III), Tl(III), Hg(II), Cd(II), Zn(II), Pb(II), Ni(II) and Co(II).

TAMH is generally preferred because the complex formation takes place at lower pH and there is a marked colour change from blue, blue-green or green to yellow or yellow-orange at the equivalence point. The difference in colour between the H_2R^+-form of TAMR and its metal complexes, especially those of bismuth(III) and thallium-(III), which are preferentially titrated at pH 1–2, is not great.

The following determinations have been investigated.

Determination of copper(II) and indium(III). Add 6–8 drops of 0·1% methanolic solution of TAMH and 20 ml of buffer (pH 4·5) to 100 ml of sample solution containing 3–30 mg of copper(II) or 6–35 mg of indium(III) and titrate the solution with 0·05*M* EDTA. The colour change at the equivalence point is from blue-green to yellow, passing through light green, and occurs with 1–2 drops of titrating solution.

When TAMR is used a buffer of pH 6·0 is preferable and the colour change is then from red to bright yellow. At higher concentrations of copper(II) the colour change is less distinct. This indicator is not recommended for indium(III) titration.

Determination of bismuth(III) and thallium(III). The titration of bismuth(III) (10·5–63 mg) is carried out at pH 1·5–2 in solutions containing nitrate. When TAMH is used there is a sharp colour change from green to yellow-orange at the equivalence point, but with TAMR there is a less suitable change from red to yellow-orange.

Carefully neutralize the thallium(III) (34–135 mg) solution with 10% ammonia until a precipitate just appears and then add 20 ml of 1*M* chloroacetic acid and a few drops of indicator solution. The equivalence point is indicated by a sharp colour change green to yellow over one drop of 0·05*M* EDTA when TAMH is used. With TAMR the colour change from brick red to yellow-orange is not quite so sharp.

Determination of mercury(II), cadmium(II), zinc(II) and lead(II). Add 20 ml of buffer (pH 6) and 6–8 drops of indicator solution to 100 ml of metal-ion solution. A very distinct colour change is obtained with both indicators at the equivalence point, *i.e.*, from blue-green to yellow (yellow-orange) when TAMH is used or from red to yellow in the presence of TAMR, over a wide range of metal-ion concentrations.

Determination of nickel(II) and cobalt(II). Add 20 ml of buffer (pH 6) and 6–8 drops of indicator solution to 100 ml of metal-ion solution containing 3–30 mg of metal ion. Heat the solution to 50–60° for nickel(II) or 60–70° for cobalt(II) and instantly titrate with 0·05*M* EDTA. A reasonably sharp colour change is observed at the equivalence point; from blue through violet to yellowish orange with TAMH and from red to yellow with TAMR.

Precision

The precision of the titrations of various metal ions at different concentrations is given in Table IV. The results were evaluated according to the procedure of Dean and Dixon[12] from 6 titrations per metal and for 95% probability.

Acknowledgement—The authors are indebted for the pure indicator samples to Ing. V. Svoboda and Ing. L. Bendová and appreciate the interest shown by Ing. V. Svoboda.

Zusammenfassung—2-(2-Thiazolazo)-5-methoxyphenol (TAMR) und 2-(2-Thiazolazo-34-methoxyphenol (TAMH) bewehren sich als gute Metallindicatore bei den ÄDTA-Titrationen, wobei TAMH einige Vorteile zeigt. Die analytische Reaktionsfähigkeit gegen Metallionen und der pH-Einfluss auf die Extinktion der Indikatorlösungen und deren Chelate mit einigen Metallen werden studiert und die Dissoziationskonstanten der Indicatore sowie auch optische Angaben für einige Metallchelate werden angeführt.

Résumé—2-(2-Thiazolylazo)-5-methoxyphénol (TAMR) et 2-(2-Thiazolylazo)-4-methoxyphénol (TAMH) s'est revelé comme indicateurs des ions métallique au cours des titrations par EDTA où TAMH s'est montré plus advantageux. L'influence du pH sur la densité optique des solutions des indicateurs et leur chelates métallique st les qualités analytiques des ces deux indicateurs sont étudié et les constants de dissociation des indicateurs et les donnés optiques des quelques chelates métalliques sont présentés.

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ISOLATION OF THORIUM IN BIOLOGICAL SAMPLES*

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Summary—A scheme for the isolation of subpicogram to microgram amounts of thorium from bone and soft tissue samples is described. Thorium is first collected by co-precipitation with iron(III) hydroxide and then adsorbed by a cation-exchange resin column from a concentrated hydrochloric acid solution of the precipitate. A double precipitation is necessary for bone samples whereas a single precipitation suffices for liver samples. The thorium is eluted from the column with an ammonium carbonate solution which is then evaporated to dryness to effect the isolation. Good recoveries of thorium from bone samples are obtained.

NUMEROUS studies have been made on the distribution and excretion of thorium compounds; these have been ably summarized by Boecker.[1] The quantity of thorium distributed over the body varies with the mode of administration and the form in which the material is injected. Mobilization usually occurs soon after administration but in many cases the amount distributed is very small, the bulk of that added remaining at the original site. The two principal sites of deposition of the mobile material are the liver and the skeleton.

Studies with animals can be carried out rather easily with the aid of γ-active thorium-234. However, in cases of exposure to the stable isotope, and more specifically in the case of those patients to whom thorotrast had been administered, the problem of measuring thorium levels is not simple.

Because thorium phosphate is one of the few acid-insoluble phosphates, the element must be separated from phosphate before any of the colorimetric or fluorimetric methods may be used for measurement. In biological samples, it would be expected that separation from bone would present the greatest difficulty. It was the purpose of this work to develop a separation scheme to isolate the smallest measurable quantities of thorium from relatively large amounts of bone with the expectation that the same scheme would be applicable to any other biological sample. The quantitative estimation of the thorium could then be made by any of the numerous methods available, for all interfering ions would have been eliminated

In this work thorium-234 (UX_1) was used without added carrier for the smallest quantities of thorium. In testing the suitability of the separation scheme for a subsequent colorimetric estimation, sufficient carrier thorium was added to the radioisotope, and the final recoveries were measured both by radioactivity and colorimetry. Menis *et al.*[2] have used both cation- and anion-exchange columns for eliminating interferences in their spectrophotometric determination of thorium. Their work is

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not strictly comparable with that described here because the levels of the impurities (5 mg of phosphate, 1 mg of iron) are very different from those encountered in samples of bone and liver.

EXPERIMENTAL

Apparatus

Radioactivity measurements were made on a Radiation Instrument Development Laboratory Model 49–51 counter with a sodium iodide crystal well. A Beckman DU quartz spectrophotometer was used for spectrophotometric measurements.

Materials

Thorium-234. The radioisotope ^{234}Th (UX_1) was prepared as needed by the method of Berman *et al.*[3] Approximately 60 g of UO_3 were dissolved in 150 ml of conc. hydrochloric acid and poured through 350 g of Amberlite XE-117 resin in a column 3·5 × 100 cm. The radioisotope was stripped whenever needed by passing 750 ml of 9·6*M* hydrochloric acid (4 + 1 conc. acid and water) through the column, evaporating off the acid and igniting the residue at 450°. The stock solution of the isotope was prepared by dissolving the residue in 100 ml of nitric acid (1 + 1).

Biological samples. Pre-ashed beef bone and several different kinds of fresh liver were used for samples. A standard quantity of 10 g of bone ash was spiked with an appropriate quantity of thorium and placed in a muffle furnace for 5 hr at 600°. Liver samples were spiked, dried at a low temperature and gradually brought up to the final temperature of 600°.

Iron(III) chloride solution. Conc. hydrochloric acid (1 ml) was added to 1 g of iron(III) chloride hexahydrate and diluted to 100 ml. Analytical grade reagents and deionized water were used.

Procedure for bone

Dry-ash the bone at 600° overnight. Dissolve 10 g of the ash in about 200 ml of 6*M* hydrochloric acid (1 + 1 conc. acid and deionized water) with heating. Add 10 ml of iron(III) chloride solution. Add concentrated ammonia solution until the pH is between 3·15 and 3·4 and collect the precipitate on a Whatman No. 40 filter paper. No washing is necessary. Dissolve the precipitate by pouring about 150 ml of 6*M* hydrochloric acid through the filter paper and collect the solution in the original beaker. Adjust the pH of the solution to 3·3 with 40% sodium hydroxide solution and repeat the collection and dissolution of the precipitate with 6*M* hydrochloric acid, collecting the solution again in the original beaker.

Pass the hydrochloric acid solution through a prepared cation-exchange resin column at a rate of about 15 drops per min. Wash the column successively with 150 ml of 6*M* hydrochloric acid and 150 ml of 20% ammonium chloride solution. Elute the thorium from the column with 75 ml of 20% ammonium carbonate solution. Cover the beaker with a ribbed watch glass and evaporate the carbonate solution to dryness. Add 1 ml of conc. sulphuric acid and heat until all the acid is expelled. Place the beaker in a muffle furnace at 450° for 1 hr, cool it, add about 5 ml of dilute nitric acid (previously made up to pH 2·0) and warm the beaker. Transfer the contents to a 10-ml volumetric flask with the pH 2·0 nitric acid solution. Take an appropriate aliquot for analysis.

Procedure for liver and soft tissue

Quantities of about 10 g have been treated. Dry the sample in a platinum dish and gradually increase the temperature to 600°. Heat for at least 5 hr. Dissolve the residue in 100 ml of 6*M* hydrochloric acid, heating if necessary. Add 10 ml of iron(III) chloride solution and adjust the pH to 3·3 with 40% sodium hydroxide. Collect the precipitate on a Whatman No. 40 filter paper, dissolve the precipitate with 6*M* hydrochloric acid and continue with the cation-exchange as in the procedure for bone.

Preparation of column

The column used was of borosilicate glass 15 mm in diameter and 450 mm long with a 10-mm coarse sintered glass disk and a Teflon stop-cock. An enlarged section was attached to the top end of the column so that a substantial amount of solution could be poured in at one time. Approximately 25 g of air-dried Dowex 50-X8 resin (50–100 mesh) was added to some deionized water and poured into the column. The column was back-washed with deionized water to remove all air bubbles, and the following solutions were passed through successively.

(1) 25 ml of 20% ammonium carbonate solution
(2) 100 ml of 20% ammonium chloride solution
(3) 100 ml of dilute hydrochloric acid (10 ml of conc. acid/100 ml)

(4) 100 ml of hydrochloric and nitric acids (50 ml of conc. hydrochloric acid and 2 ml of conc. nitric acid /100 ml)
(5) 100 ml of 6*M* HCl (1 + 1 mixture of conc. acid and deionized water).

DISCUSSION

It might be expected that quadrivalent thorium would be strongly absorbed by a cation-exchange resin[4], but thorium-234 was removed only to the extent of 50% by a 30-g Dowex 50-X8 resin column from a 6*M* hydrochloric acid solution of 10 g of bone ash. Attempts to use a nitric acid solution with an anion-exchange resin column were equally unsuccessful, and it was necessary to use a preliminary separation step to remove the bulk of the phosphate. Precipitation of thorium along with a collecting precipitate was the method chosen, and ordinary filtration was used although centrifugation would have been equally satisfactory. A double precipitation was necessary for bone samples because the first precipitate contained sufficient phosphate to cause interference with the cation-exchange separation (40 to 50% not retained by the column). Even in the case of liver, a single preliminary precipitation was necessary before the cation-exchange column could be used. The conditions used for the liver were exactly the same as for the second precipitation in the case of bone samples.

The preliminary separation

The object of the preliminary separation is to separate the thorium from the bulk of the phosphate. Sill and co-workers[5] have reported the successful use of barium sulphate to collect the thorium from as much as 2 g of bone in solution even in strongly acidic media. In the present work, all the separations were based on 10-g bone ash samples, and the acidity was very much a factor in the quantity of thorium collected by barium sulphate. The addition of 4 ml of 0·2*M* barium chloride to the bone dissolved in 150 ml of 6*M* hydrochloric acid, followed by the addition of sulphate resulted in the collection of only 2·5% of the thorium at the tracer level. The addition of 3 ml of 2*M* sulphuric acid to precipitate some calcium sulphate from the acidic bone-solution resulted in the collection of about 2% of the thorium. When the bone solution was partially neutralized by the addition of concentrated ammonia solution until a calcium phosphate precipitate just persisted (pH 1·88) and then the barium chloride solution and sodium sulphate solution were added successively, 97·3% of the thorium was collected. However, the barium sulphate collection was not suitable for the subsequent ion-exchange separation because of its insolubility in acid.

Attempts to use a limited amount of calcium phosphate precipitate as a collector were not satisfactory because of the difficulty in controlling the amount of precipitate. The addition of iron(III) and the adjustment of the pH to a definite value proved to be the best solution. The control of pH is essential because exceeding the upper limit results in the precipitation of a large amount of calcium phosphate which increases the bulk considerably. Too low a pH gives poor collection. The first precipitation carries sufficient phosphate to interfere with the ion-exchange absorption of the thorium, so double precipitation is necessary. Recovery of carrier-free thorium-234 from both collection steps was essentially complete. A single preliminary collection for liver adequately removed the excess of phosphate.

Final separation

Sorption of thorium on a cation-exchange resin (Dowex 50-X8) from a fairly concentrated hydrochloric acid solution was used for the final stage of the separation

because thorium is almost selectively removed under these conditions. Complexing agents which would reduce the charge of quadrivalent thorium should be absent. None of the usual cations found in biological materials would be retained on a cation-exchange resin in the presence of 6*M* hydrochloric acid. Iron(III), for example forms a negatively charged chloride complex. Phosphate, which forms complexes with thorium, would be expected to be almost completely in the form of undissociated phosphoric acid, but the quantity from 10 g of bone ash is sufficient to interfere with the ion-exchange step, and has to be reduced as already described. The optimum quantity of resin was determined from the study of the retention of thorium in the presence of that concentration of phosphate still in solution after the preliminary separation. The thorium from a solution containing 4 ml of 85% phosphoric acid (equivalent to the quantity of phosphate in 10 g of bone ash) was first collected by 40 mg of iron precipitated at pH 3·3. The precipitate was separated and dissolved in 6*M* hydrochloric acid, and the solution was poured through columns containing different amounts of resin. The results are shown in the Table I. For the routine procedure a 25-g column was used.

TABLE I.—RETENTION OF THORIUM ON ION-EXCHANGE COLUMNS OF VARYING SIZE

Weight of resin, g	Th passed through, %
5	32
10	8·4
15	3·4
20	0·5

For stripping the thorium from the column, 20% ammonium carbonate solution as described by Chernikhov *et al.*[6] was used. The rate of elution seemed quite variable but in general most of the activity was removed from the column in the first 50 ml. Table II shows 3 separate elution patterns. The eluate was collected in 25-ml portions.

TABLE II.—ELUTION OF THORIUM BY AMMONIUM CARBONATE

Portion	Eluted, %		
	Run 1	Run 2	Run 3
1	84·1	86·8	48·3
2	5·1	11·6	49·6
3	7·0	0·3	0·8
4	0·1	—	—
Total	96·3	98·7	98·7

The use of ammonium carbonate for elution is very desirable because it is completely eliminated during the evaporation process. Ammonium chloride solution was used to remove the acid from the column before the addition of the carbonate solution because it too could be eliminated by low-temperature heating. Sulphuric acid was added before the final heating in order to convert the thorium into the sulphate form which is stable at 450° and easily soluble. The final heating temperature of 450° was sufficient to eliminate traces of organic matter eluted from the column and also permit the use of borosilicate beakers.

With the separation scheme employed, only thorium should be isolated from biological samples. Radioactivity measurements showed essentially complete recovery. As a final check to see whether the separation scheme would produce samples suitable for some chemical method, a series of bone samples was spiked with both radioactive thorium and stable thorium. The colorimetric method using Morin, as described by Fletcher and Milkey,[7] was employed as a check on the radioactivity measurement, The recoveries measured by the two methods are shown in Table III. It was noticed

TABLE III.—RECOVERY OF THORIUM FROM BONE

Sample No.	Recovery, %	
	Radioactivity	Colorimetric
1	99·2	97·1
2	101·7	100·7
3	99·9	99·3
4	99·2	98·2

that the colorimetric method gave high results if the hydroxylamine were omitted. This was attributed to the presence of traces of iron introduced with reagents added after the separation.

Since the thorium is finally isolated in a soluble form, the final measurements may be made by any method. This is in contrast to schemes which use an insoluble collecting agent such as barium sulphate which requires an alkaline solution of a complexing agent for dissolution. The measurement must then be made under alkaline conditions.

Résumé—On décrit un schéma d'isolement de quantités de thorium allant du subpicogramme au microgramme à partir d'os et de tissus mous. On recueille d'abord le thorium par coprécipitation avec l'hydroxyde de fer(III), puis l'adsorbe sur une colonne de résine échangeuse de cations à partir d'une solution du précipité dans l'acide chlorhydrique concentré. Une double précipitation est nécessaire pour les échantillons d'os alors qu'une précipitation simple suffit pour les échantillons de foie. Le thorium est élué de la colonne par une solution de carbonate d'ammonium que l'on évapore alors à sec pour effectuer l'isolement. On obtient de bonnes récupérations de thorium à partir des échantillons d'os.

Zusammenfassung—Ein Verfahren zur Isolierung von Subpicogrammbis Mikrogrammengen Thorium aus Proben von Knochen- und Weichteilgewebe wird beschrieben. Zuerst wird das Thorium durch Mitfällung mit Eisen(III)-hydroxid gesammelt und anschließend aus einer Lösung des Niederschlages in konzentrierter Salzsäure an einer Säule aus Kationenaustauscherharz adsorbiert. Für Knochenproben ist zweimalige Fällung notwendig, für Proben aus Leber genügt eine. Das Thorium wird von der Säule mit einer Ammoncarbonatlösung eluiert, die zur Isolierung zur Trockne eingedampft wird. Bei Knochenproben werden gute Thoriumausbeuten erzielt.

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DISSOCIATION CONSTANTS AND ULTRAVIOLET SPECTRA OF THE CONJUGATE ACIDS OF OXIMES

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Summary—A spectrophotometric method was used to determine the acid dissociation constants of the conjugate acids of dimethylglyoxime and biacetyl monoxime. The dissociation constant, the acidity function and the absorbance of a mixture of protonated and unprotonated oxime were utilized to obtain the ultraviolet spectra of the protonated oxime.

Two semiquantitative determinations of the dissociation constant of the conjugate acid of dimethylglyoxine have been previously reported. Banks and Anderson[1] studied several dioximes, including dimethylglyoxime, and concluded that all the dissociation constants were approximately the same and of the order of 100 in 75% dioxane–25% water mixtures. Freiser[2] reported pK_A for dimethylglyoxime to be less than 2, *i.e.*, K_A to be greater than 0·01. No similar investigation for biacetyl monoxime has been reported.

Oximes, such as dimethylglyoxime and biacetyl monoxime, are very weak bases and decompose in acid solution.[3] Because of this, the present study utilizes a modified spectrophotometric technique to obtain more accurate results for the dissociation constants of the conjugate acids of dimethylglyoxime and biacetyl monoxime. In addition, the ultraviolet spectra of these acids have been determined.

EXPERIMENTAL

Reagents

Dimethylglyoxime (Baker analysed) was dried in a desiccator over calcium chloride and used without further purification.

Biacetyl monoxime (Matheson, Coleman and Bell) was sublimed thrice at 35° and 1 mm Hg pressure.

All other chemicals used were reagent grade.

Apparatus

All spectrophotometric measurements were made on a Cary Model 14 instrument equipped with a thermostatic cell compartment (±0·1°).

Procedure

A 3-ml portion of hydrochloric acid of known strength was transferred to a 1-cm cell by pipette. This solution was brought to constant temperature and then 0·04807 ml of a solution of either biacetyl monoxime in water or of dimethylglyoxime in ethanol was added by means of a Hamilton microlitre syringe equipped with a Chaney adapter. The absorbance was measured at a fixed wavelength at intervals of time. About 15 sec elapsed between the addition of oxime and the first recording of the absorbance. The absorbance plot was extrapolated to zero time so as to yield the absorbance of the equilibrium mixture of the undecomposed protonated and unprotonated forms of the oxime.

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RESULTS AND DISCUSSION

The procedure described was used at 50-Å intervals over the wavelength range 2100–2700 Å, and the ultraviolet spectrum of dimethylglyoxime in hydrochloric acid of various concentrations was obtained. A plot of the extinction coefficient, ε_S, of the solution *vs.* wavelength is shown in Fig. 1;

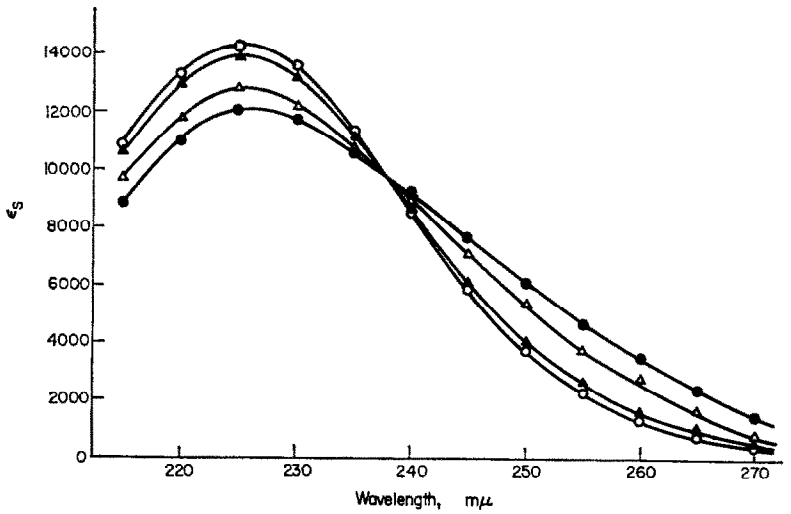


FIG. 1.—Effect of hydrochloric acid concentration on the absorption spectra of dimethylglyoxime between 210 and 270 mμ, at 25·0°C.
Isosbestic point 237·6 mμ; $\varepsilon_{237.6} = 10{,}120$.
[HCl], *M*: ○—0·0; ▲—0·406; △—1·218; ●—1·624.

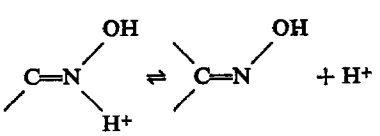
$$\varepsilon_S = \frac{A_0}{[HD]_t} \tag{1}$$

where A_0 = absorbance extrapolated to zero time
$[HD]_t$ = dimethylglyoxime initially added = $[HD] + [HDH^+]$
HD = dimethylglyoxime
HDH^+ = protonated dimethylglyoxime

Figure 2 shows a plot of ε_S *vs.* wavelength in the range 2300–2500 Å obtained in a similar way with biacetyl monoxime in hydrochloric acid of various concentrations. Both figures show very good isosbestic points indicating that the extinction coefficients of both the protonated and unprotonated oximes are not a function of solvent composition. Hence, a spectrophotometric method can be used to give accurate results for the concentrations of protonated and unprotonated oximes.

Only the method used to determine the acid dissociation constant of biacetyl monoxime will be described; the method employed for dimethylglyoxime is identical.

The acid dissociation constant for the reaction



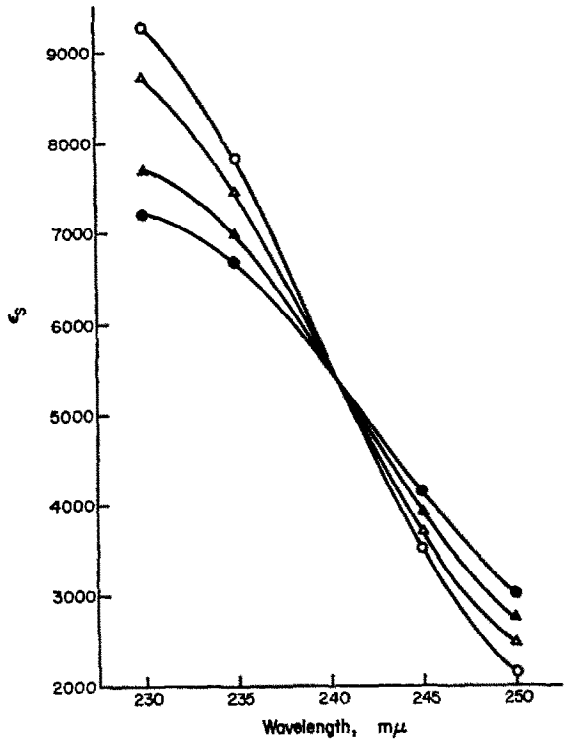


FIG. 2.—Effect of hydrochloric acid concentration on the absorption spectrum of biacetyl monoxime between 230 and 250 mμ at 25·0°C.
Isosbestic point 240·8 mμ
[HCl], *M*: ●—10·07; ▲—7·55; △—2·52; ○—0·00.

in the case of biacetyl monoxime is given by

$$K_A^{HMH^+} = \frac{a_{H^+}a_{HM}}{a_{HMH^+}} = \frac{h_0[HM]}{[HMH^+]}, \qquad (2)$$

where a denotes the activity of the species indicated by the subscript. It is readily seen that a plot of the ratio, $[HMH^+]/[HM]$ *vs.* h_0, the acidity function, should result in a straight line whose slope is the dissociation constant, $K_A^{HMH^+}$.[4]

Acidity functions were used because of the high ionic strengths involved. The values of h_0 used[5] are shown in Tables I and II.

The values of $[HMH^+]/[HM]$ were obtained from equations (3) and (4) as follows:

$$A_0 = A_{HM} + A_{HMH^+} = \varepsilon_{HM}[HM] + \varepsilon_{HMH^+}[HMH^+] \qquad (3)$$

$$[HM]_1 = [HM] + [HMH^+] \qquad (4)$$

$$\varepsilon_S = \frac{A_0}{[HM]_1}. \qquad (5)$$

The value of ε_{HM} was determined in neutral solution where decomposition does not take place and there is no significant protonation. The value of ε_{HMH^+} was obtained by plotting ε_S *vs.* h_0 and extrapolating to infinite h_0. At infinite h_0, *i.e.*, infinite concentration of hydrochloric acid, all of the biacetyl monoxime will be in the protonated form and hence ε_S becomes ε_{HMH^+}. Figure 3 shows an example of the extrapolation

TABLE I.—EXTINCTION COEFFICIENT OF DIMETHYLGLYOXIME AS A FUNCTION OF HYDROCHLORIC ACID CONCENTRATION

No.	[HCl] M	h_0	ε_S^{2250} 20°C	ε_S^{2250} 25°C	ε_S^{2250} 30°C	[HDH⁺]/[HD] 20°C	[HDH⁺]/[HD] 25°C	[HDH⁺]/[HD] 30°C
1	5·70	101·7	5698	11170	5673	10·4	13·4	10·8
2	5·48	84·8	5761	11000	5823	9·59	10·6	8·93
3	5·15	64·9	6005	—	6061	7·28	—	6·88
4	4·72	45·3	6361	10440	6399	5·27	5·89	5·13
5	4·00	25·1	7243	9495	7218	2·92	3·11	2·97
6	3·65	19·0	7712	8913	7675	2·27	2·30	2·31
7	3·40	15·5	8163	8388	8182	1·82	1·80	1·81
8	2·87	10·0	9214	7400	9120	1·14	1·17	1·18
9	2·25	6·27	10580	5923	10410	0·622	0·628	0·669
10	1·81	4·15	—	4973	11310	—	0·403	0·437
11	1·07	1·78	12640	3565	12570	0·191	0·164	0·200

TABLE II.—EXTINCTION COEFFICIENT OF BIACETYL MONOXIME AS A FUNCTION OF HYDROCHLORIC ACID CONCENTRATION

No.	[HCl] M	h_0	ε_S^{2275} 20°C	ε_S^{2275} 25°C	ε_S^{2275} 30°C	[HMH⁺]/[HM] 20°C	[HMH⁺]/[HM] 25°C	[HMH⁺]/[HM] 30°C
1	11·85	21900	6091	6176	6133	∞	54·3	116
2	11·38	13650	6248	6329	6310	23·4	15·4	16·1
3	10·91	8710	6453	6553	6519	9·14	7·05	7·54
4	10·43	5755	6733	6886	6762	4·63	3·58	4·38
5	10·14	4470	6914	6986	6943	3·38	3·05	3·23
6	9·95	3550	7086	7100	7124	2·61	2·58	2·48
7	9·74	3090	7233	7286	7143	2·14	2·02	2·41
8	9·48	2480	7405	7419	7419	1·73	1·79	1·70
9	9·10	1780	7662	7681	7695	1·28	1·26	1·23
10	8·76	1330	7914	7962	7857	0·959	0·914	1·02
11	8·28	902	8205	8219	8119	0·688	0·680	0·760
12	7·44	452	8676	8676	8548	0·379	0·381	0·452

from which it can be seen that ε_S asymptotically approaches a limiting value. In effect, equation (3) becomes

$$\varepsilon_S = \frac{A_{HMH^+}}{[HMH^+]} = \varepsilon_{HMH^+}. \tag{6}$$

At 20, 25 and 30°, the values of ε_{HMH^+} were found to be 6070, 6120 and 6110 respectively. The values of [HM] and [HMH⁺] were then calculated from equations (3) and (4) and the ratio [HMH⁺]/[HM] was obtained. The results for biacetyl monoxime are shown in Table II and for dimethylglyoxime in Table I.

The plot of [HMH⁺]/[HM] *vs.* h_0 results in a straight line except at very high values of [HMH⁺]/[HM], as shown by the typical example in Fig. 4. It is difficult to obtain highly accurate values of A_0 at high acid concentrations where there is a concomitant increase in the rate of decomposition of the oximes; errors in A_0 result in errors in the values of ε_{HMH^+} and of [HMH⁺]/[HM]. The errors involved in the extrapolation are not large; ε_S will be reasonably accurate even at high acid concentrations and thus ε_{HMH^+} should be reasonably accurate. However, small errors in

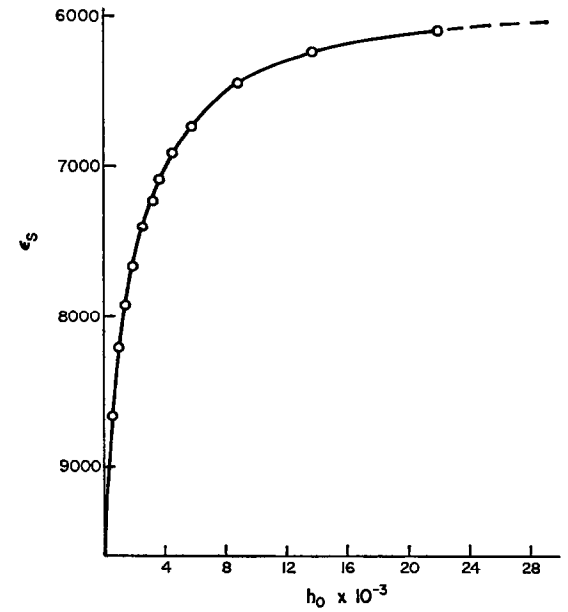


FIG. 3.—Molar absorptivity of biacetyl monoxime as a function of the acidity, at 2·0°C. $\varepsilon^{2275}_{HMH^+} = 6070.$

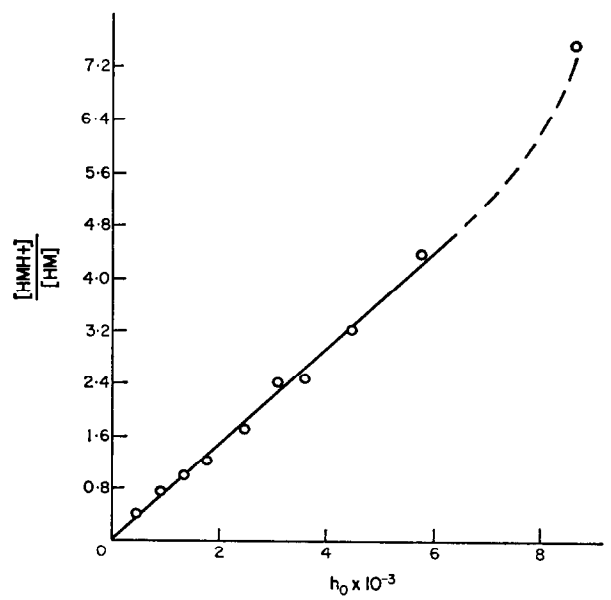


FIG. 4.—The dissociation constant of biacetyl monoxime at 30·0°C.

$$K_A^{HMH^+} = \frac{h_0[HM]}{[HMH^+]} = 1380.$$

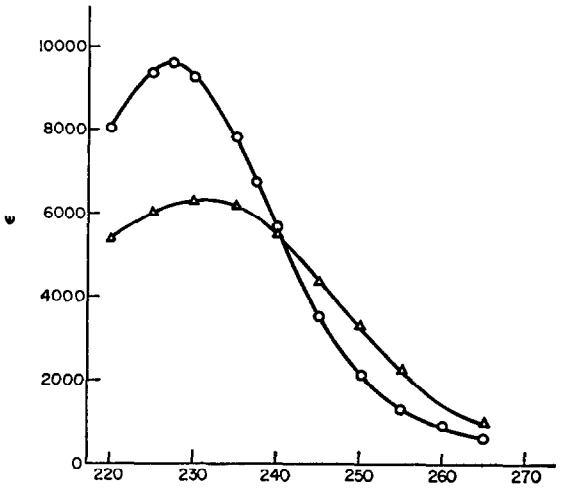


FIG. 5.—The ultraviolet absorption spectra of protonated and unprotonated biacetyl monoxime.
○—HM; λ_{max} 227·5 mμ; ε_{max} 9650
△—HMH^+; λ_{max} 231·0 mμ; ε_{max} 6300.

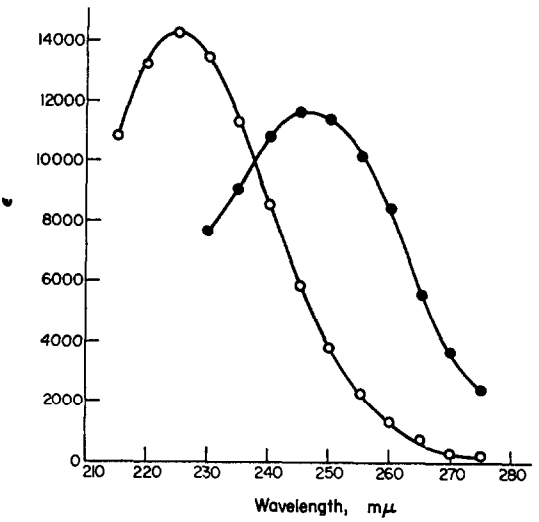


FIG. 6.—The ultraviolet absorption spectra of protonated and unprotonated dimethylglyoxime.
○—HD; λ_{max} 225·0 mμ; ε_{max} 14100
●—HDH^+; λ_{max} 246·0 mμ; ε_{max} 10800.

A_0 will produce large errors in [HMH^+]/[HM] when this ratio is very large, and when the acid concentration is high, because the error in A_0 will approach or exceed the value of A_{HM} as A_{HM} becomes very small. Hence, the straight-line portion of a plot, as shown in Fig. 4, was always obtained by ignoring the [HMH^+]/[HM] values for high acid concentrations.

TABLE III.—THE DISSOCIATION CONSTANTS $K_A^{HDH^+}$ AND $K_A^{HMH^+}$

Temperature, °C	$K_A^{HDH^+}$	$K_A^{HMH^+}$
30·0	8·69	1380
25·0	8·67	1440
20·0	8·72	1490

The values obtained for the dissociation constants, $K_A^{HMH^+}$ and $K_A^{HDH^+}$, are given in Table III. (The values of ε_{HDH^+} were found to be 11830 and 4900 at 2550 Å and 2250 Å respectively.)

A value of ε_{HMH^+} at any given wavelength can be obtained from the dissociation constant, equations (2), (3) and (4), and a single value of ε_S obtained at the same wavelength. Values of ε_{HMH^+} were thus calculated at 50-Å intervals for the region 2200–2650 Å. The calculated spectrum for protonated biacetyl monoxime is shown in Fig. 5 along with the spectrum of the unprotonated monoxime. The same procedure was used to obtain the spectrum for protonated dimethylglyoxime in the region 2300–2750 Å, and the results are shown in Fig. 6. A red shift of 210 Å is observed on protonation of dimethylglyoxime, and a red shift of 35 Å for biacetyl monoxime. This red shift has been observed previously in the protonation of other more basic Schiff's bases.[3,6]

Acknowledgement—The authors acknowledge the partial assistance of the United States Atomic Energy Commission in supporting this investigation, under Contract AT(11-1)582.

Résumé—On a utilisé une méthode spectrophotométrique pour déterminer les constantes de dissociation acide des acides conjugués de la diméthylglyoxime et de la diacétyl monoxime. On a utilisé la constante de dissociation, la fonction d'acidité et l'absorption d'un mélange d'oxime protonée et non protonée pour obtenir le spectre ultra-violet de l'oxime protonée.

Zusammenfassung—Die Säuredissoziationskonstanten der konjugierten Säuren von Dimethylglyoxim und Biacetylmonoxim wurden spektrophotometrisch gemessen. Die Dissoziationskonstante, die Aciditätsfunktion und die Extinktion einer Mischung von protoniertem und nicht protoniertem Oxim wurden benutzt, um die Ultraviolettspektren des protonierten Oxims zu erhalten.

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DETERMINATION OF ALUMINIUM AND SODIUM IN TUNGSTEN BY NON-DESTRUCTIVE ACTIVATION ANALYSIS

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Summary—The sodium and aluminium content of tungsten has been measured by thermal neutron activation analysis. The concentration of aluminium was evaluated from the 1·78 MeV, and that of sodium from the 2·76 MeV full energy peaks. The minimum detectable concentrations of impurities were 0·04 μg of aluminium and 0·07 μg of sodium per 100 mg of tungsten.

TUNGSTEN is known to be a poor matrix for activation analysis. The reactions induced by thermal neutrons in natural tungsten are listed in Table I.[1,2] Owing to ^{187}W interference, the sensitivity of the non-destructive method is inadequate for elements

TABLE I.—INTERFERING (n, γ) REACTIONS IN TUNGSTEN

Natural stable isotopes	Abundance %	Isotopic cross-section *barn*,	Species	Half-life	Decay	Stable final product
^{180}W	0·14	20	^{181}W	140 d	k, β^-, γ	^{181}Ta stable
^{184}W	30·7	2	^{185m}W	1·8 min	IT	^{185}Re stable
			^{185}W	73 d	β^-	
^{186}W	28·7	34	^{187}W	24 h	β^-, γ	^{187}Re stable

which do not emit γ-rays with energy above 1 MeV. The non-destructive method was used by Corth for the determination of 0·1–10% of tantalum in tungsten and for sodium by Reuland and Voight.[3,4] In the tungsten samples analysed by the authors the concentration of aluminium was found to be 3–5 $\times$ 10^{-4} %, that of sodium 2–8 $\times$ 10^{-4} %.

EXPERIMENTAL

Irradiations were carried out in the VVRSz-type reactor with 5 $\times$ 10^{12} n/cm^2/sec thermal neutron flux. The cadmium ratio, as measured in aluminium, was 1:30 at the site of exposure, which was connected to the measuring equipment by means of a pneumatic tube system.[5] The helical tungsten samples, 80–100 mg in weight were kept in danamide (polyamide) holders during the exposure. For the activity measurement the irradiated holders were replaced by nonactivated ones. For samples of this size the attenuation of the neutron flux in tungsten is less than 1% and its effect can be neglected. Solutions of aluminium nitrate (0·1% Al) and sodium sulphate (0·5% Na) dropped onto Düren 640 m 5·5-cm filter paper (0·02 mg ash content) were used as standards, and the measured values were corrected for the impurities present in the filter paper.

An NaI crystal, 3 in. $\times$ 3 in. (Nuclear Enterprises 12/IA-4/12 Integral Assembly) and an NTA-256 type multichannel analyser and a single channel analyser were used for the activity measurements. In order to reduce the pile-up of signals due to the high tungsten activity, the signal width of the photomultiplier was reduced from 18 μsec to 1·5 μsec by decreasing the plate load resistance. Even so, the superimposed tungsten background was still too high in the region of the 2·76 MeV photopeak of sodium. To overcome this, the distance between sample and detector was increased (the individual activity counts decrease linearly with the solid angle, whereas the pile-up counts

decrease at least with the square of the solid angle) and a lead shield was inserted between sample and detector (the higher energy gamma intensity of the measured activity is decreased less by the shield than is that of the tungsten radiation, and the pile-up is known to be proportional at least to the second order of the transmission probability). By variation of the distance from sample to detector and of the thickness of lead, the ratio of the measured activity to the total interfering activity can be increased so as to render the tungsten pile-up comparable to the natural background count. Under the given experimental conditions a 20-cm sample–detector distance and 1·5 cm of lead was enough to provide a good aluminium to tungsten pile-up ratio. To reduce the natural background, the measurements were performed in an iron box with a wall 15 cm thick lined with lead, cadmium and copper plates.

RESULTS

Aluminium

The nuclear reaction

$$^{27}\mathrm{Al}(n, \gamma)^{28}\mathrm{Al} \xrightarrow[\beta-]{t_{1/2} = 2{\cdot}27 \text{ min}} {}^{28}\mathrm{Si} + \gamma$$

with 0·23 barn cross-section for thermal neutrons was used for the determination of aluminium. The measurement covered the 1·775 MeV gamma activity from ^{28}Si.[1,2] Calculations made from the available cross-section[6] and fast neutron flux data have shown that the chance of ^{28}Al production by the fast neutron induced ^{28}Si(n, p)^{28}Al and ^{31}P(n, α)^{28}Al is negligible, considering that 60 μg of silicon or 170 μg of phosphorus contamination would be necessary to produce as much ^{28}Al as 1 μg of aluminium. Though either of these high contaminations seemed improbable, parallel irradiations were performed with a cadmium filter. The check proved that the total ^{28}Al activity originated from ^{27}Al.

Both the samples and standards were irradiated for 60 sec. On termination of the irradiation 10 sec were needed to take the sample to the measuring equipment and 40 sec to replace the sample holder before the start of the activity measurement. In serial analysis, for maximum statistical accuracy the counts in the aluminium full energy peak area were taken on a single channel analyser for 200 sec,[7] at two 100-sec intervals to check the half-life. After the total decay of the aluminium activity, which takes 20 min, the tungsten and other background activities could be established. The aluminium concentration was evaluated from the sample and standard full energy peak counts. The method was checked by measuring the half-life and the pulse-height spectrum of both the sample and the standard on the multichannel analyser. In Fig. 1a the spectrum of a 90-mg tungsten sample containing 0·4 μg of aluminium, and the background of the tungsten after the decay of the aluminium, are shown, while in Fig. 1b the spectrum of this sample is shown with that of a 10-μg aluminium standard corrected for background. In Fig. 2 is shown the decrease with time of the aluminium photopeak counts, corrected for background in the tungsten sample. The value of the half-life thus obtained is in agreement with the 2·27 min half-life of the ^{28}Al activity.

The results were also checked by performing the measurement described above with measured amounts of 1–10 μg of aluminium juxtaposed to the samples. The result of the activity measurement showed in each case the total measured aluminium concentration to be equal to the sum of the amount already found in the tungsten and the juxtaposed amount of aluminium.

Since the standards and samples were not irradiated simultaneously, the time behaviour of the reactor flux had to be checked. The reproducibility of the measurements was tested also by reactivating the tungsten samples after several days. For

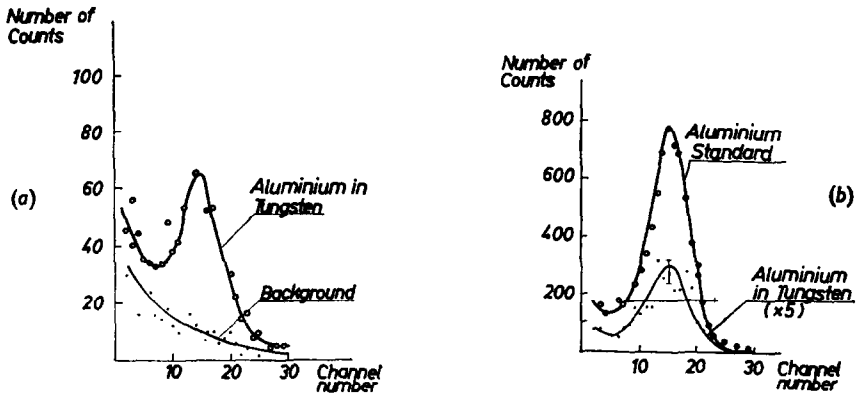

FIG. 1.—(a) Spectra of a 90-mg tungsten sample, containing 0·4 μg of aluminium, and of the background of the tungsten after decay of the aluminium. (b) Spectra of the same sample and of a 10-μg aluminium standard corrected for background.

tungsten samples containing 4–6 ppm of aluminium (0·3–0·5 μg) the results were found to be reproducible within the 10% statistical variation in the number of counts.

The maximum obtainable sensitivity for the non-destructive method is determined by the background count. In the present case it was equivalent to 0·1 μg of aluminium. If the minimum detectable amount is defined such that the counts due to the activity

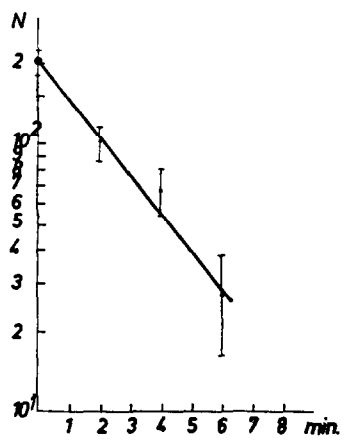

FIG. 2.—The decay of the aluminium full energy peak in a 90-mg tungsten sample containing 0·4 μg of aluminium.

of the element to be determined should exceed the experimental error of the background count (taken as three times the standard deviation) the method permits the quantitative determination of 0·04 μg of aluminium in 100 mg of tungsten.

Sodium

For the determination of sodium, the tungsten samples were irradiated for 200 sec. The activity measurement was based on the 15 hr half-life ^{24}Na produced by the ^{23}Na(n, γ)^{24}Na reaction (0·505 barn reaction cross-section).[1,2] No inconvenient interference was caused by the fast neutrons. Since the analysis is sensitive for even small

amounts of sample (20–100 mg), the method can be applied to cover both elements even if the inhomogeneity of the contaminants along the tungsten filament must also be known. For the identification of sodium, the 2·76 MeV full energy peak was used because the 1·38 MeV peak was considerably masked by the pile-up of the tungsten activity. The samples were measured twice, each time for 2500 sec, to check the

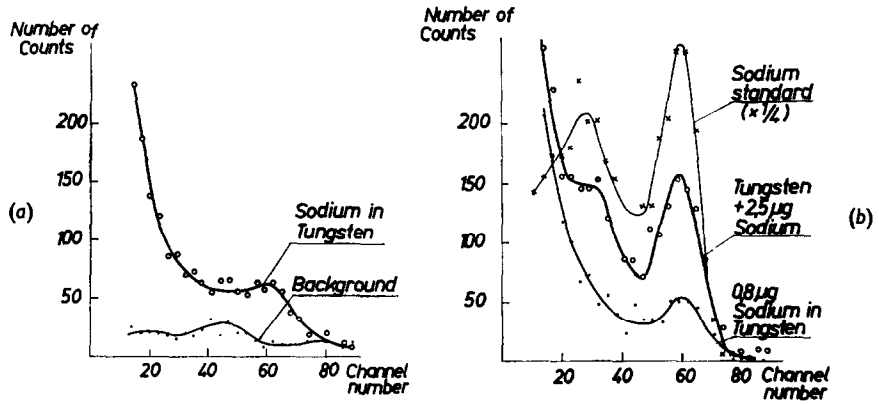

FIG. 3.—(a) Spectra of an 88-mg tungsten sample containing 0·8 μg of sodium and of the background. (b) Spectra of the same sample, alone and with 2·5 μg of sodium juxtaposed, and of a 20-μg sodium standard.

half-life. The spectrum and background are plotted in Fig. 3a for an 88-mg tungsten sample containing 0·8 μg of sodium. The spectra of an 88-mg tungsten sample, of 2·5 μg of sodium juxtaposed to the tungsten and corrected for background, and of a 20-μg sodium standard are shown in Fig. 3b. The results were checked by the same measurements as for aluminium.

The background counts are equivalent to 0·2 μg of sodium and the minimum detectable quantity is 0·07 μg of sodium, if a 1-hr count is used.

Zusammenfassung—Es wurde der Natrium- und Aluminiumgehalt von Wolfram durch thermische Neutronenaktivierungsanalyse bestimmt. Die Aluminiumkonzentration wurde aus der Full-Energy-Peak von 1,78 MeV, die von Sodium aus der von 2,76 MeV berechnet. Minimal nachweisbare Konzentration der Verunreinigung erwies sich als 0,04 μg für Aluminium und 0,07 μg für Natrium.

Résumé—L'aluminium et le sodium ont été dosés dans le tungstène au moyen de l'analyse par activation par neutrons thermiques. Les concentrations sont évaluées du pic de 1,78 MeV pour l'aluminium et du pic de 2,76 MeV pour le sodium. La détectabilité minime est 0,04 μg d'aluminium et 0,07 μg de sodium par 100 mg de tungstène.

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CHARACTERIZATION AND ANALYSIS OF WAXES BY DIFFERENTIAL THERMAL ANALYSIS

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Summary—The characterization of waxes by differential thermal analysis is described. An endothermic peak at 475–480° is characteristic of microcrystalline and polyethylene waxes, and measurement of its area provides a method for the estimation of these waxes in mixtures.

RECENT interest in the characterization of paraffin and microcrystalline waxes and in the analysis of mixtures of these waxes is typified by the papers by Ferris,[1] Fox,[2] Templin[3] and Ludwig.[4] Lange and Jochinke[5] have applied differential thermal analysis (DTA) to a study of the melting and solidification of waxes (temperature range 20–140°) and suggest that these curves may be used to characterize a wax and in many cases to determine the components of a mixture. We have similarly applied DTA but, in our case, in the range 20–600°.

From our studies of the melting curves we draw the same general conclusions as Lange and Jochinke and suggest that, to a possibly limited extent, these curves may be used to characterize a wax. The melting curves do not give unequivocal criteria for distinguishing between microcrystalline and polyethylene waxes and paraffin waxes, but there is a tendency for most microcrystalline and polyethylene waxes to be characterized by a single melting endotherm (Fig. 2), whereas the paraffin waxes show at least two endotherms (Fig. 1). Exceptions to this tendency are the Superla 165/170° and Jasber 180/185° waxes (*e* and *h*, Fig. 2) and the 140/145° *ex* Assam and the 56/58° German Zeitz waxes (*f* and *j*, Fig. 1). The additional peaks in the paraffin wax traces may be due to the crystalline transition orthorhombic → hexagonal which Ludwig detected by infrared spectra.

DTA in the extended temperature range up to 600° does, however, provide a ready means of distinguishing between microcrystalline and polyethylene waxes and paraffin waxes. At the higher temperatures all the paraffin waxes showed broad diffuse peaks which returned to baseline before 460°. In contrast, a sharp peak at 475–480° is characteristic of all the microcrystalline and polyethylene waxes which we have examined. This peak may be used to identify the presence of a microcrystalline or polyethylene wax in a mixture and also to give a quantitative estimation of the amount present; thus Table I shows the results obtained by measuring the area of this peak and relating it to the amount of microwax C700 in an artificial mixture of this microwax and the paraffin wax 135/140° *ex* Stanlow Refinery. The DTA trace of the mixture containing 50·0% of microwax is reproduced in Fig. 3.

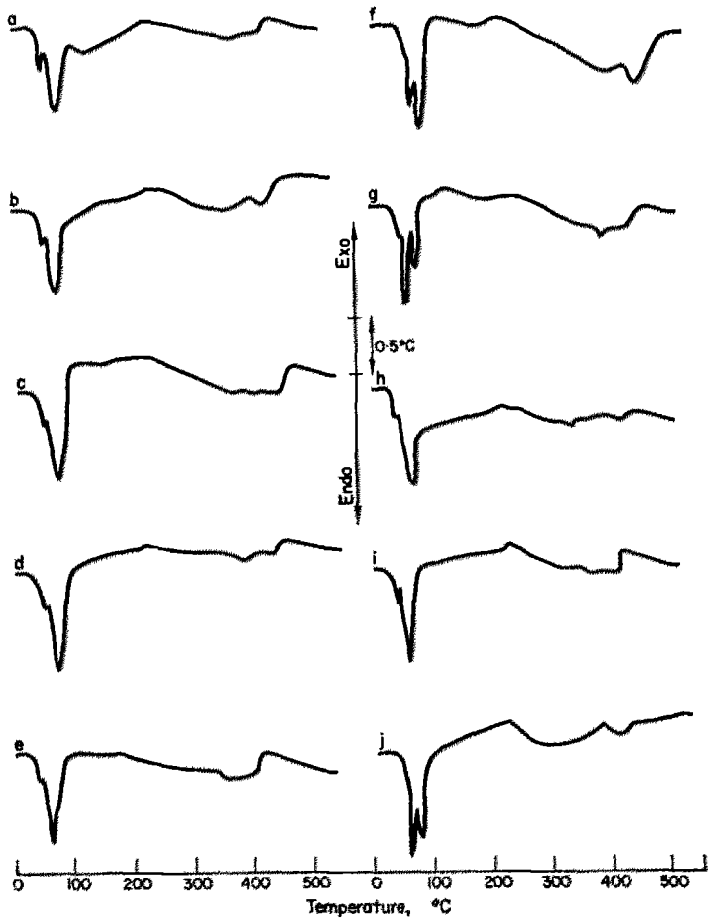

FIG. 1.—DTA curves of paraffin waxes.
a, 135/140 *ex* Stanlow Refinery, sample 1; *b*, 135/140 *ex* Stanlow Refinery, Sample 2; *c*, 140/145 *ex* Stanlow Refinery, sample 1; *d*, 140/145 *ex* Stanlow Refinery, sample 2; *e*, 120/125 *ex* B.P. Trading Co; *f*, 140/145 *ex* Assam; *g*, 135/140 *ex* Assam; *h*, 52/54 Russian; *i*, 52/54, German, Kopsen Webau; *j*, 56/58 German, Zeitz.

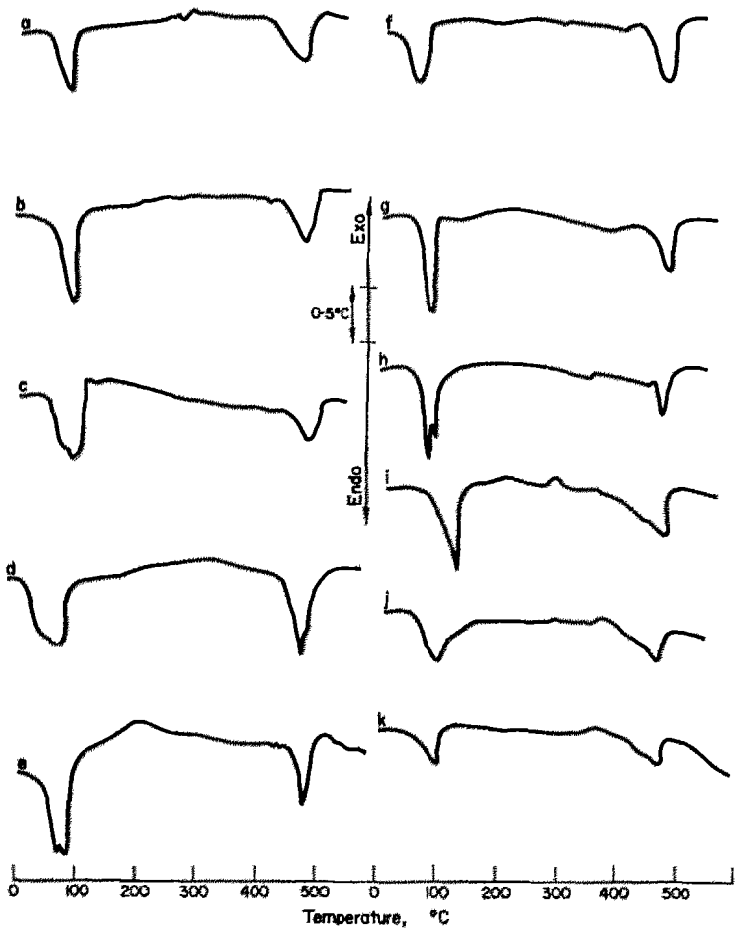

FIG. 2.—DTA curves of micro and polyethylene waxes.
a, Microwax C23; *b*, Microwax C700; *c*, Superwax Amber 180°; *d*, Starwax Amber 180°; *e*, Superla 165/170; *f*, Superla 165/170; *g*, Bareco Amber; *h*, Jasber 180/185°; *i*, Polyethylene PA130; *j*, Polyethylene AC 629; *k*, Polyethylene AC6.

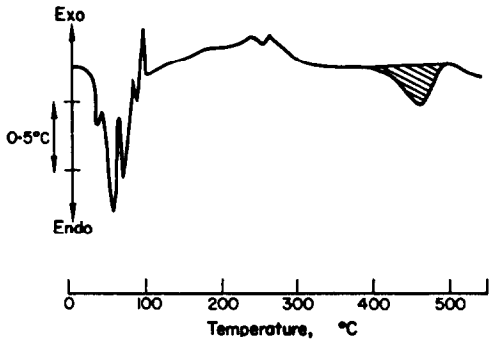

FIG. 3.—DTA curve of 1:1 mixture of microwax C23 and paraffin wax 135/140 *ex* Stanlow Refinery.
The shaded area gives a measure of the amount of microwax present (see Table 1).

TABLE I.—TYPICAL RESULTS OBTAINED IN THE ANALYSIS OF MIXTURES OF MICROWAX C700 AND PARAFFIN WAX 135/40 *ex* STANLOW REFINERY

Microwax present, %	Microwax found by measuring the area of the peak at 475°, %
71·9	67·3
50·0	53·9
47·2	51·6
19·2	15·6

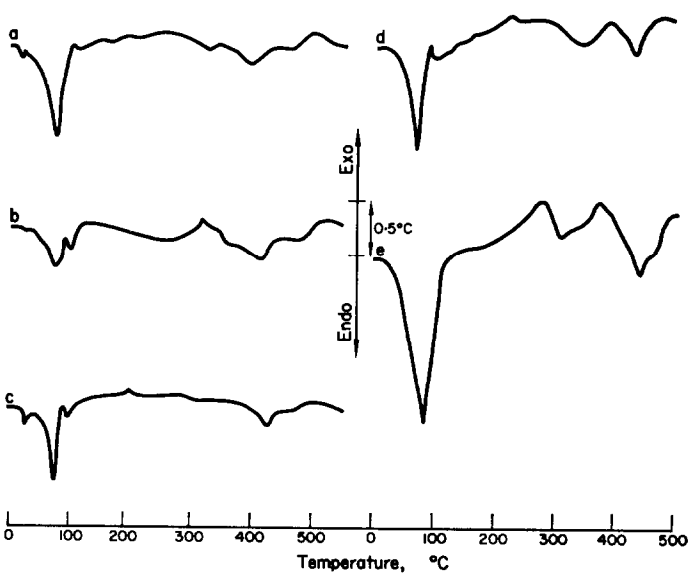

FIG. 4.—DTA curves of waxes.
a Hoechst Wax L; *b*, Hoechst Wax OM; *c*, Candelilla Wax; *d*, Beeswax; *e*, Carnauba Flake.

To provide a comparison the DTA traces of some other waxes are included (Fig. 4). These include the natural waxes Beeswax, Candelilla and Carnauba Flake and the synthetic Hoechst waxes L and OM.

These results are preliminary; a full evaluation of the limitations of this method of analysing wax mixtures will be carried out when we have finished a programme of work designed to define the limitations of DTA as a quantitative method; factors to be taken into account will include variations in the size and thermal conductivity of the samples, heating rate, crucible design and methods of packing.

EXPERIMENTAL

The apparatus used was the American Instrument Co. DTA instrument. The sample (~100 mg) and reference material (calcined alumina) were contained in inconel cups, the bases of which rested on chromel-alumel thermocouples; the cups were supported in an inconel block. Differential temperature was plotted against block temperature on an Aminco X–Y recorder. All runs were carried out at a heating rate of 8°/min.

To obtain maximum reproducibility in the quantitative experiments the same components, *i.e.*, cups, block and furnace, were used throughout. The pair of cups used were chosen to be as nearly as possible of the same weight.

Acknowledgements—We wish to acknowledge the generosity of the American Instrument Co. in providing the DTA equipment on loan, and also the experimental assistance given by Mr. P. Stevenson, who carried out many of the runs.

Zusammenfassung—Die Charakterisierung von Wachsen durch Differentialthermoanalyse wird beschrieben. Ein endothermer Peak bei 475–480° ist charakteristisch für mikrokristalline und Polyäthylenwachse; Messung seiner Fläche bietet eine Methode zur Bestimmung dieser Wachse in Gemischen.

Résumé—On décrit la caractérisation de cires par analyse thermique différentielle. Un pic endothermique à 475–480° est caractéristique de cires microcristallines et polyéthyléniques et la mesure de son aire fournit une méthode d'estimation de ces cires dans des mélanges.

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TITRIMETRISCHE GOLDBESTIMMUNG MIT ASCORBINSÄURE UNTER VISUELLER ENDPUNKTSINDIKATION

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Zusammenfassung—Es wurde eine reduktometrische Methode zur Gold(III) bestimmung mit Ascorbinsäure mit visueller Indikation ausgearbeitet. Den Endpunkt zeigt das Verschwinden der orangenen Farbe des Tetrabromoaurat(III). Störende Ionen werden durch Extraktion mit Äthylacetat abgetrennt und anschliessend Gold(III) nach Zusatz von Kaliumbromid in der organischen Phase titriert. Das entstehende farblose Dibromoaurat(I) kann nach Zusatz von Variaminblau als Indikator zu metallischem Gold weitertitriert werden, das sich als feine Schicht an der Grenze der Phasen abscheidet und die Indikation nicht stört.

UNTER den titrimetrischen Goldbestimmungsmethoden[1,2] findet man nur wenige, bei denen Gold(III)ionen unmittelbar und mit visueller Endpunktsindikation erfaßt werden. Bei einer dieser Methoden[3] dient das Verschwinden der gelben Farbe des Tetrachloroaurat(III)ions, bei einer anderen,[4] das des braunen Tetrabromoaurats(III) nach Einwirkung der reduzierenden Maßlösung zur Wahrnehmung des Endpunkts. Gold(III) wird in beiden Fällen zu Gold(I) reduziert. Infolge der schwachen Farbe des Chlorokomplexes gibt die erste Methode in verdünnten Lösungen keine zuverlässigen Ergebnisse. Ein Nachteil der zweiten Methode liegt darin, daß bei mindestens 95° titriert werden muß. In der Praxis hat keines dieser Verfahren besondere Bedeutung. Milazzo[5] schlug eine Titration mit Hydrochinon mit *o*-Dianisidin als Indikator vor. Die Bildung von kolloidalem Gold stört jedoch oft das Wahrnehmen der Farbänderung des Indikators.

Nachdem wir eine potentiometrische Methode zur Titration von Gold(III) mit Ascorbinsäure[2] ausgearbeitet hatten, wurde eine visuelle Endpunktsindikation angestrebt.

Die Versuchsbedingungen wurden schon bei der potentiometrischen Bestimmung eingehend untersucht. Gold(III)ionen können in 0,01-und 0,001m Lösungen im pH-Bereich von 1,6 bis 3,00 gut titriert werden, sofern die Chloridkonzentration nicht mehr als 1m beträgt. Gearbeitet wird bei ungefähr 50°, da hier einerseits die Reduktion schneller verläuft, andererseits die bei der Oxydation der Ascorbinsäure entstehende Dehydroascorbinsäure noch keinen meßbaren Fehler verursacht.

EXPERIMENTELLER TEIL

Lösungen und Reagenzien

Gold(III)chlorid—Stammlösung, 0,1n. Metallisches Gold wird in Königswasser gelöst, die Lösung mehrmals eingedampft. Vor Verdünnung wird soviel Salzsäure zugesetzt, daß sich die Wasserstoffionenkonzentration der Lösung zwischen 0,5n und 0,1n bewegt. Der Goldgehalt wird gravimetrisch sowohl durch Reduktion mit Eisen(II)sulfat, wie mit Ascorbinsäure bestimmt. Durch entsprechende Verdünnung 0,01- und 0,001n Lösungen werden bereitet.

Ascorbinsäuremasslösung 0,1n. Ascorbinsäure (8,9 g) werden in dest. Wasser gelöst, mit 100 mg ÄDTA als Stabilisator versetzt und mit Wasser auf 1 l. ergänzt. Das benutzte dest. Wasser soll in einer Glasapparatur destilliert werden.[6] Der Gehalt der Lösung wird mit Kaliumjodat gegen Variaminblau bestimmt.[7,8] Durch Verdünnung werden 0,01- und 0,002n Lösungen bereitet. Der Faktor der verdünnten Lösungen wird täglich zweimal, vor und nach den Bestimmungen ermittelt. Es genügt jedoch den Wirkungswert von 0,01n Ascorbinsäurelösungen täglich einmal zu kontrollieren, sofern die Lösung in Flaschen mit Glasstopfen vom Licht geschützt aufbewahrt wird. Über die Wirkungswertänderung von 0,01n Ascorbinsäurelösungen wurde schon früher eingehend berichtet.[8]

Wäßrige Kaliumbromidlösung, 10%*ige*

Äthylacetat analysenrein

Variaminblau Indikator. Zehn g des unter dem Namen Variaminblau B als Farbstoff dienenden Handelsproduktes werden in 200 ml heissem Wasser gelöst, die Lösung mit 0,4 g Ascorbinsäure und 1,5 g Aktivkohle versetzt und heiß filtriert. Zum farblosen oder höchstens schwach gelben Filtrat werden 50 ml gesättigte Natriumchlorid-Lösung gegeben. Nach Abkühlen filtriert man die ausgeschiedenen weissen Nadelkristalle, wäscht mit kaltem Wasser und trocknet im Vakuum bei Zimmertemperatur. Der gereinigte Indikator wird in gut schliessender Flasche aufbewahrt. Vom Indikator bereitet man entweder eine 0,5% ige wäßrige Lösung, die fünf Tage lang brauchbar ist, oder man verreibt ihn mit Natriumchlorid im Verhältnis 1:100 und benutzt ihn in dieser unbegrenzt haltbaren festen Form.

TITRATION VON GOLD(III)IONEN IN GEGENWART VON KALIUMBROMID

Die farblose oder schwach gelbe Gold(III)chloridlösung wird nach Bromidzusatz je nach dem Goldgehalt orange bzw. rötlichbraun. Diese Farbe entwickelt sich rasch, die Stabilität des entsprechenden Komplexes ist bei niedrigem pH hoch. Mit zunehmender Chloridkonzentration nimmt zwar die Farbintensität der Lösung ab, dies stört aber nur bei der photometrischen Bestimmung. Das Redoxpotential des Chlorokomplexes liegt höher als das des Bromokomplexes; dementsprechend reagiert zuerst der Chlorokomplex mit der Maßlösung. Beim Verschwinden der Farbe des Bromokomplexes liegen demnach keine meßbaren Mengen von Gold(III)-ionen mehr in der Lösung vor.

Das Normalredoxpotential des farbigen Tetrabromoaurat(III)-komplexes beträgt +0,87 V. Mit geeigneten Reduktionsmitteln, z.B. Ascorbinsäure läßt sich die Verbindung leicht in farbloses instabiles Dibromoaurat(I) überführen. Sowohl bei Einwirkung von überschüssigem Reduktionsmittel, wie auch durch Disproportionierung wird metallisches Gold gebildet. Somit tritt in der auf Farblosigkeit titrierten Lösung allmählich wieder eine Farbvertiefung ein. Da aber die Disproportionierung unter dem gegebenen Bedingungen erst nach 5–10 Minuten merklich wird, kann Ascorbinsäure zur Titration verwendet werden.

Man gibt 5–20 ml der ungefähr 0,003m Gold(III)ionenlösung in einen 100-ml Titrierkolben, setzt 5 ml 10%ige Kaliumbromid-Lösung hinzu und ergänzt mit Wasser auf 40 ml. Die so vorbereitete braunrote Lösung vom pH-Wert 1–1,5 titriert man bei Zimmertemperatur mit 0,01n Ascorbinsäure bis Farblosigkeit. Die Ergebnisse sind in Tab. I. dargestellt.

Die Titration ist in 0,3–0,1m salzsaurer Lösung und bei Zimmertemperatur am genauesten. In 1m salzsaurer Lösung liegt die Genauigkeit noch innerhalb ±3% sofern bei 40–50° gearbeitet wird.

An Fremdionen stören Cadmium-, Blei-, Arsen-, Aluminium-, Zink-, Calzium-, Barium- und Alkaliionen in Mengen von *ca.* 200 mg nicht. Bei Silbermengen unter 50 mg stört der entstehende Niederschlag die Endpunktsindikation nicht. Quecksilber(II)ionen stören ebenfalls nicht, nur ist in ihrer Gegenwart eine 3–5 fache Menge von Kaliumbromid zuzusetzen.

Farbige Ionen wie Platin(IV), Kupfer(II), Kobalt, Nickel, Chrom(III), Eisen(III) stören, da der Endpunkt nicht sichtbar ist. Es stören weiterhin Oxydationsmittel, die Bromid zu Brom oxydieren oder deren Redoxpotential positiver ist als das des Golds und die deshalb Maßlösung verbrauchen. In diesen Fällen muß das Gold vorher abgetrennt werden.

EXTRAKTION VON GOLD(III)-IONEN MIT ÄTHYLACETAT UND TITRATION IN DER ORGANISCHEN PHASE

Die Extraktion mit Äthylacetat in salzsaurer Lösung bietet eine gute Trennung des Golds von den störenden Metallionen. Demgegenüber können in bromwasserstoffsaurer Lösung störende Ionen mitextrahiert werden, z.B. Eisen(III)bromid. In der organischen Phase wird das Gold ohne weiteres reduktometrisch mit visueller Indikation erfaßt.

TABELLE I.—TITRATION VON GOLD(III)-IONEN IN GEGENWART VON KALIUMBROMID ALS INDIKATOR MIT 0,01n ASCORBINSÄURE
Au(III) → Au(I)

Eingewogen, Au(III) *ml*	Maßlösung-verbrauch, *ml*	Mittelwert, *ml*	Sollwert, *mg*	Gold gefunden, *mg*	Abweichung, %
	3,40				
	3,45				
5,00	3,43	3,43	3,51	3,38	−3,7
	3,43				
	3,43				
	3,45				
	7,00				
	6,99				
10,00	7,00	7,00	7,02	6,90	−1,7
	7,02				
	7,00				
	7,00				
	10,56				
	10,56				
15,00	10,58	10,57	10,53	10,41	−1,2
	10,56				
	10,58				
	10,58				

Die beste Extraktion erfolgt bei 5% Salzsäuregehalt; höhere Konzentrationen sind für die anschliessende Titration ungünstig. Die besten Titrierergebnisse werden erzielt, wenn aus 0,5–1m salzsaurer Lösung extrahiert wird.

Die zu bestimmende Lösung wird in einen 100 ml Scheidetrichter gegeben, wenn nötig mit 20 ml Wasser ergänzt und mit soviel Salzsäure versetzt, daß sich die Säurekonzentration der Lösung zwischen 0,5–1m einstellt. Dann gibt man 20 ml Äthylacetat hinzu und schüttelt kräftig 1 Minute durch. Nachdem sich die zwei Phasen getrennt haben, läßt man die wäßrige Phase in einen zweiten Scheidetrichter ab und wiederholt die Extraktion mit 10, dann mit 5 ml Äthylacetat. Trennen sich die zwei Phasen nur langsam, so ist die wäßrige Lösung nicht genügend sauer; dann sind noch 1–2 ml 1m Salzsäure zuzusetzen.

Die Äthylacetat-Phasen sammelt man in einem mit Glasstopfen versehenen 100-ml Erlenmeyer-Kolben. Nötigenfalls wäscht man vorher die gesammelten Phasen im Scheidetrichter mit 1m Salzsäure. Dann setzt man 10 ml 10%ige Kaliumbromidlösung hinzu, und titriert mit 0,01n Ascorbinsäurelösung unter kräftigem Zusammenschütteln der beiden Phasen solange, bis im durchfallenden Licht die Emulsion milchartig weiß wird. 1 ml 0,01n Ascorbinsäurelösung entspricht 985 μg Gold. Am Ende der Titration liegt quantitativ der Dibromoaurat(I) Komplex vor.

Die auf die beschriebene Weise titrierte Lösung wird nach Zusatz von Variaminblau durch Bildung der oxydierten Form des Indikators ß. Titriert man weiter mit Ascorbinsäure, so werden zuerst die in der wäßrigen Phase anwesenden Gold(I)ionen zu elementarem Gold reduziert. Zeitweise verschwindet die blaue Farbe. Sie erscheint erneut nach Vermischen der beiden Phasen, wenn ein Teil der Gold(I)ionen von der organischen wieder in die wäßrige Phase übergeht. Es ist solange zu titrieren bis der Indikator nach grau umschlägt und auch nach Zusammenschütteln der Phasen nicht wieder blau wird. Das entstehende Gold befindet sich als dünne Schicht an der Grenze der beiden Phasen und stört die Indikation nicht. Wenn man in reinwäßriger Lösung mit Ascorbinsäure zu kolloidalem elementaren Gold titriert, stört dieses die Endpunktsindikation.

TABELLE II.—TITRATION VON GOLD(III)-IONEN NACH ÄTHYLACETAT EXTRAKTION MIT 0,01n ASCORBINSÄURE

Gold Sollwert, *mg*	Fremdionen, *mg*	Maßlösung verbrauch, *ml* (a)	(b)	Gold gefunden, *mg* (a)	(b)
		3,45	1,74	3,40	3,43
3,51	—	3,45	1,73	3,40	3,40
		3,43	1,76	3,38	3,46
		4,42	—	4,35	—
		4,42	—	4,35	—
		4,44	—	4,37	—
4,38	—	4,43	2,24	4,36	4,41
		4,43	2,28	4,46	4,49
		4,42	2,25	4,35	4,43
	—	7,05	3,50	6,94	6,89
	—	7,00	3,48	6,89	6,86
	—	7,01	3,58	6,90	7,05
	Pt^{4+}:30	7,38	—	7,27	—
7,02	Cu^{2+}:50	7,28	—	7,17	—
	Se^{4+}:50	7,16	—	7,05	—
	Pb^{2+}:50	7,12	—	7,01	—
	Te^{4+}:50	7,20	—	7,09	—
	Ag^{+}:30	7,12	—	7,01	—

(a) In Gegenwart von Br^- ionen bis$[AuBr_2]^-$
(b) Dann weitertitriert in Gegenwart von Variaminblau bis Metallgold.

In Tab. II sind die Ergebnisse dargestellt. Sie zeigen, daß nach Extraktion des Tetrachloroaurat(III) mit Äthylacetat Gold sowohl im Gegenwart von Kaliumbromid, als von Variaminblau gut titrierbar ist. Im ersten Fall beträgt das Äquivalentgewicht Mol/2. Bei Fortführung der Titration in Gegenwart von Variaminblau läßt sich das erste Ergebnis gut kontrollieren. Das Äquivalentgewicht beträgt bei der Variaminblautitration Mol/3.

Goldmengen von ungefähr 500 μg können aus salzsaurer Lösung in Gegenwart von Platin, Kupfer, Selen, Tellur, Blei usw. mit Äthylacetat extrahiert und mit 0,002n Ascorbinsäure gegen Variaminblau mit einem Fehler von 2–5 % titriert werden.

Summary—A reductometric method for the determination of gold(III) with ascorbic acid has been developed. The end-point is given by the disappearance of the orange colour of the tetrabromoaurate(III) ion. Interfering ions may be separated by extraction with ethyl acetate and then the gold(III) titrated in the organic phase after the addition of potassium bromide. The colourless dibromoaurate(I) which is formed can be further reduced to metallic gold (Variamine Blue used as indicator) in which case the gold precipitates as a thin layer at the boundary of the phases, and does not interfere with the indicator.

Résumé—On a élaboré une méthode réductométrique de dosage de l'or (III) au moyen d'acide ascorbique. Le point de fin de dosage est donné par la disparition de la coloration orangée de l'ion tétrabromoaurate (III). On peut séparer les ions gênants par extraction à l'acétate d'éthyle et doser alors l'or (III) dans le phase organique après addition de bromure de potassium. Le dibromoaurate (I) incolore qui se forme peute encore être réduit à l'état d'or métallique (le Bleu Variamine étant utilisé comme indicateur), auquel cas l'or précipite à l'état de couche mince à la séparation des phases, et n'interfère pas avec l'indicateur.

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SHORT COMMUNICATIONS

Assay for 9-acridanone in urban atmosphere by thin-layer chromatography fluorimetric procedures

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In a previous paper the column and thin-layer chromatographic separation of polynuclear ring-carbonyl compounds was described.[1] These methods were applied to the development of a group of methods for the analysis of the carcinogen, 7*H*-benz(de)anthracen-7-one, in urban atmospheres.[2] These earlier investigations indicated that other ring-carbonyl compounds are present in urban atmospheres. This paper represents proof that 9-acridanone is a constituent of polluted urban atmospheres. Several methods involving two-dimensional thin-layer chromatography and fluorimetry are presented for the assay of this compound.

EXPERIMENTAL*

Reagents and apparatus

Solvents were obtained in the purest grades and were distilled if there was any evidence of interfering impurities. 9-Acridanone was obtained from K and K Laboratories, Plainview, New York, and crystallized to a constant melting point.

Spectrophotofluorimetry. An Aminco-Bowman spectrophotofluorimeter with 0·1- and 1-ml cells was used with the following settings: sensitivity 50, slit arrangement No. 2, and phototube RCA type IP 21. The fluorescence spectra of spots on thin-layer chromatograms were obtained by use of an Aminco solid-sample accessory.[1,3]

Procedure

A 1–2 mg sample of a benzene-soluble extract of airborne particulates was separated two-dimensionally on aluminia—cellulose (2:1). Some of the developing solvents used in the alternative separation methods were toluene-methanol (9:1, v/v) followed by dimethylformamide—water (35:65), and toluene—ether (7:3) followed by dimethylformamide—water (35:65). In another method alumina was used as the adsorbent with ethyl acetate—cyclohexane (1:1) as the developer in both dimensions. 9-Acridanone (0·5 to 1 μg) was run with each one-dimensional separation. The two-dimensional separation took about 3–4 hr. The appropriate spots were scraped from the plate. Standards and the unknown were eluted from the adsorbent with methanol—trifluoroacetic acid (4:1). Three min of shaking were required. The elution took about 10 min. The solutions of the standards and the unknown were evaporated and then diluted to an appropriate volume (0·1–1 ml) with methanol—trifluoroacetic acid (4:1). The excitation and emission spectra of the standards and unknown were determined. Analysis was at F 390/450. The whole operation took 3·5–4·5 hr.

The calculations are based on the equation

$$\mu\text{g of 9-acridanone/g of benzene-soluble fraction} = \frac{1000 \cdot W_s \cdot R_x}{W_{bs} \cdot R_s}$$

where the final volumes of standard and unknown are identical and $W_s = \mu$g of standard 9-acridanone, R_x = product of meter multiplier and transmittance readings obtained for unknown, R_s = product of meter multiplier and transmittance readings obtained for standard, and W_{bs} = weight (in mg) of benzene-soluble fraction placed on plate.

DISCUSSION

The greatest loss of 9-acridanone resulted when the compound was eluted from the plate following development. The variations in adsorbent or developer had little effect on the recovery (Table I).

* Mention of commercial products does not constitute endorsement by the Public Health Service.

TABLE I.—RECOVERY OF 9-ACRIDANONE FROM THE PLATE AFTER DEVELOPMENT

Adsorbent	Developer	Recovery %	Average recovery %
1. Al_2O_3–cellulose (2:1)	Toluene–methanol (9:1)	55, 61, 68, 71, 66	64
2. Al_2O_3–cellulose (2:1)	Dimethylformamide–water (35:65)	62, 64, 63, 70, 66, 62, 61, 60, 74	65
3. Al_2O_3–cellulose (2:1)	Toluene–ether (7:3)	58, 61, 50, 73	61
4. Al_2O_3	Ethyl acetate–cyclohexane (1:1)	60, 65, 69, 69, 60, 62, 60, 58	63

The type of separation obtained and the large assortment of other fluorescent spots present on the chromatogram are depicted in Fig. 1. All samples were assayed in acidic methanol. In this solution 9-acridanone was present as the neutral compound in the ground state (as shown by the fluorescence excitation spectrum) and as the cationic salt in the excited state (as shown by the fluorescence emission spectrum) (Fig. 2). The advantage of this type of analysis is the large wavelength separation between the fluorescence excitation wavelength maximum at 390 mμ and the emission wavelength maximum at 455 mμ. Because of this wide separation, scatter is less of a problem and the analysis is performed more readily.

The characterization of 9-acridanone was based on the R_f values of standard and unknown being identical in the various adsorbents and developers studied. In addition the extract of the unknown spot gave fluorescence spectra identical to those of 9-acridanone in the various solvents (Fig. 2).

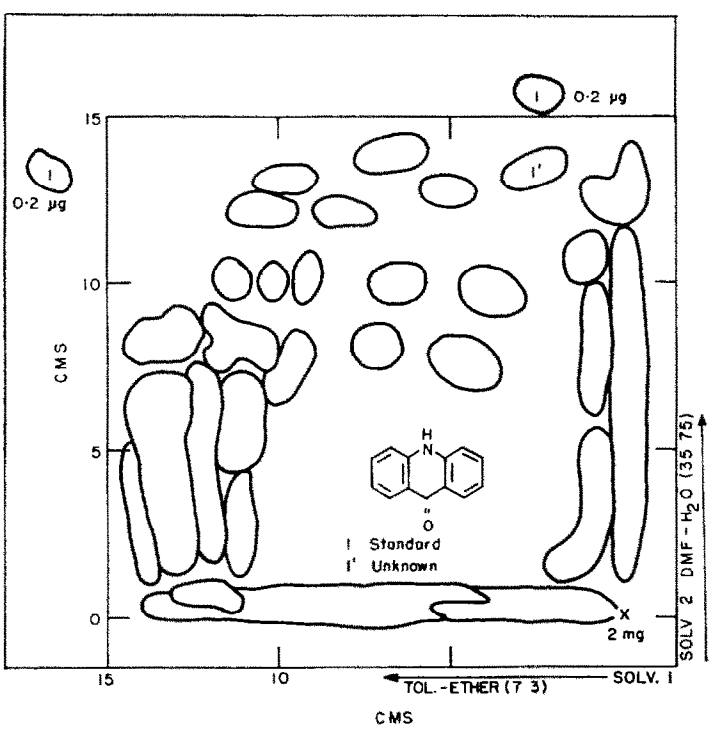

FIG. 1.—Two-dimensional thin-layer chromatogram on alumina-cellulose (2:1), toluene–ether (7:3) in first direction and dimethylformamide–water (35:65) in second direction. 9-Acridanone (0·2 μg) run in each direction: 2 mg of benzene–soluble fraction of airborne particulates separated.

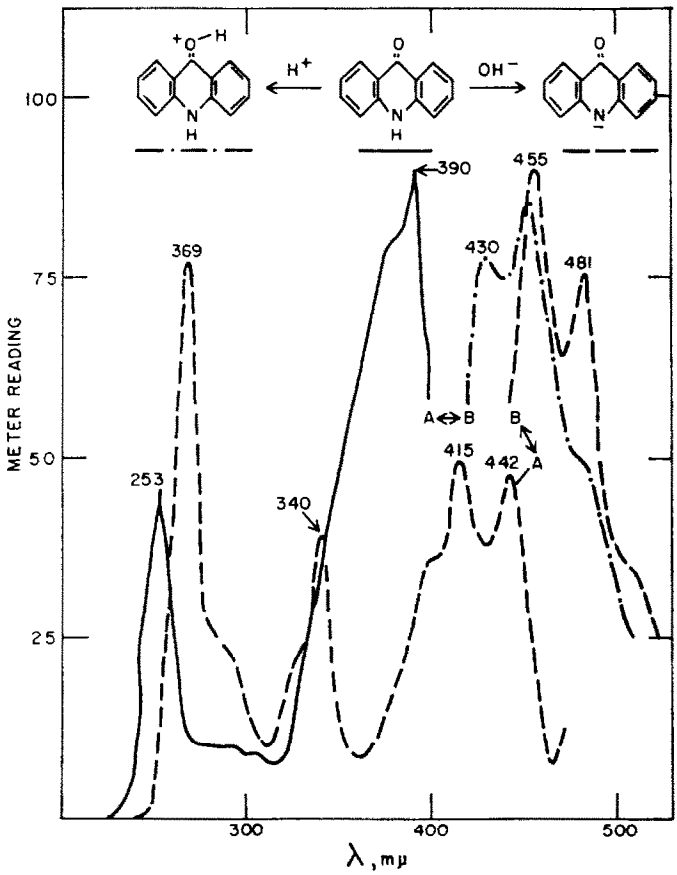

FIG. 2.—Spectrophotofluorimetric excitation (A) and emission (B) spectra of 0·2 μg of 9-acridanone/ml of solution at meter multiplier setting 0·01.
(– – –) In dimethylformamide containing 5% of 10% aqueous tetraethylammonium hydroxide solution, F 269/481. Excitation (———) and emission (– · – ·) spectra of 9-acridanone in methanol-trifluoroacetic acid (4:1) at F 390/450.

TABLE II.—COMPARISON OF METHODS OF ASSAY FOR 9-ACRIDANONE IN A COMPOSITE URBAN ATMOSPHERIC SAMPLE

Separation method*	Benzene solution μg/g	Mean	Airborne particulate sample μg/g	ng/m³ of air
1. 1 → 2	40, 40, 35, 40	40	3	0·4
2. 3 → 2	40, 30, 40, 40	40	3	0·4
3. 4 → 4	60, 20, 50	40	3	0·4
4. 1 → 2†	60, 50, 40, 30	45	4	0·5

* See Table I.
† Direct spectrophotofluorimetric assay[1,3] after treatment of spot with 5 μl of trifluoroacetic acid, F 390/460.

A composite airborne particulate sample was analysed with the help of two-dimensional thin-layer chromatography and fluorimetry either after elution or directly from the plate (Table II). Several different development methods were compared. The alumina—cellulose elution methods gave the best results; the direct fluorimetric method gave the most variable results. Either of the two alumina—cellulose elution methods is recommended for the analysis of 9-acridanone in urban atmospheres and in air pollution source effluents. Approximately 0·4 ng of 9-acridanone is present in each cubic metre of urban atmosphere.

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Summary—9-Acridanone has been found in urban atmospheres. Four two-dimensional thin-layer chromatographic methods have been described for the assay of this compound in urban atmospheres and in air pollution source effluents. Fluorimetric assay was done either directly on the plate or after elution. The best method involved two-dimensional separation on alumina-cellulose followed by elution and fluorimetric analysis of the acidic methanol solution. Urban atmospheres contain approximately 0·4 ng of 9-acridanone/m³ of air.

Résumé—On a trouvé la 9-acridanone dans les atmosphères urbaines. On a décrit quatre méthodes de chromatographie en couche mince bidimensionnelle pour la détermination du composé dans les atmosphères urbaines et les dégagements des sources de pollution de l'air. On a effectué le dosage fluorescimétrique soit directement sur la plaque, soit après élution. La meilleure méthode comprend la séparation bidimensionnelle sur alumine-cellulose suivie d'élution et de l'analyse fluorescimétrique de la solution méthanolique acide. Les atmosphères urbaines contiennent approximativement 0,4 ng de 9-acridanone par m³ d'air.

Zusammenfassung—In städtischen Atmosphären wurde 9-Acridanon gefunden. Vier zweidimensionale dünnschichtchromatographische Methoden wurden zum Nachweis der Verbindung in städtischen Atmosphären und in Emissionen aus Quellen der Luftverunreinigung beschrieben. Der fluorimetrische Nachweis wurde entweder direkt auf der Platte oder nach Elution geführt. Beim besten Verfahren wurde zweidimensional auf Aluminiumoxyd/Zellulose getrennt, eluiert und die saure Methanollösung fluorimetrisch analysiert. Stadtatmosphären enthalten ungefähr 0,4 ng 9-Acridanon pro m³ Luft.

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Determination of scandium in wolframite and in the residues obtained after the extraction of tungsten

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WOLFRAMITE contains about 0·01–0·05% of scandium. During the extraction of tungsten by the carbonate process, this scandium is enriched to about 0·03 to 0·1% in the residue, which contains mostly iron and manganese.

In the course of our investigations on the extraction of scandium from wolframite residues, it became necessary to determine the scandium content of wolframite and its residues. Though several methods are known[1–6] for the estimation of scandium very little information is available for its determination in low grade ores. The method recommended by Schoeller and Powell[7] for determination of scandium in wolfram is very tedious and involves a large number of steps. Therefore an alternative method was developed which is comparatively quick and simple and was found to be quite reliable.

Separation of scandium from iron and manganese by solvent extraction with tri-butyl phosphate (TBP)

Two of the major constituents present in wolframite residues after the removal of tungsten are iron and manganese. Preliminary experiments indicated that extraction of scandium by TBP from hydrochloric acid is complete only if the acid concentration exceeds 8*M*. Under these conditions extraction of iron also is complete, whereas only a small fraction of manganese is transferred to the organic phase (K_d values for Fe, Sc and Mn are 400, 24 and 0·2 respectively). From 2*M* hydrochloric acid the extraction of scandium is very low ($K_d < 0{\cdot}005$) whereas that of iron is sufficiently high ($K_d > 7$) to give fairly good separation from scandium.

Synthetic mixtures of iron(III), manganese(II) and scandium were prepared by taking known amounts of stock solutions and the hydrochloric acid concentration of each was adjusted to 8*M*. Each solution was shaken twice with an equal volume of TBP which had been pre-equilibrated with 8*M* hydrochloric acid. Two extractions are necessary to extract all the iron, because of its high concentration in the aqueous phase. Most of the iron is extracted in the first step and the extraction of scandium is completed only after all the iron has been removed. The two extracts are mixed and the scandium is back-extracted with an equal volume of 2*M* hydrochloric acid. It should be emphasized here that if the scandium is not back-extracted within an hour or so, recovery is incomplete. An appreciable amount of iron is also back-extracted, but most of it is removed by extraction with TBP pre-equilibrated with 2*M* hydrochloric acid (the volume used being half that of the aqueous phase). The scandium in the aqueous phase is precipitated from the hot solution by addition of ammonia solution in the presence of excess of ammonium chloride.* To reduce the manganese content still further, this step is repeated, after dissolution of the hydroxide in the minimum amount of hydrochloric acid. The precipitate is finally filtered off, dissolved in 25–50 ml of conc. hydrochloric acid and extracted with TBP, and the scandium is back-extracted with 2*M* hydrochloric acid as before. This solution is free from iron but contains traces of manganese from which it is finally freed by precipitation with ammonia in the presence of ammonium chloride, and the product is ignited to the oxide. The oxide thus obtained is found spectrographically to be 99·9% pure (Fe = 0·010%, Mn = 0·005%).

Results obtained by this procedure are summarized in Table I. It can be seen that the relative error increases with decrease in scandium content in the mixture. Also, when the amount of scandium is small the error is considerably higher, mainly because of the unfavourable gravimetric factor. Therefore the minimum amount of scandium should be 20–30 mg.

* There are some contradictory observations regarding the completion of precipitation of scandium as hydroxide by ammonia. Fisher and Bock[8] observed complete precipitation of scandium with ammonia in the absence of ammonium carbonate, whereas Vickery[9] has found low recoveries even with ammonia free from carbon dioxide. Our results, however, show that in the concentration range 20–200 mg of Sc_2O_3 per 100 ml the precipitation of scandium is more than 99·5% complete by ammonia free from carbon dioxide, even in the presence of a 50 to 100-fold excess of ammonium chloride. The ammonia precipitation method has also been used by Alimarin and Shen Han Si[3] for standardization of scandium solution.

TABLE I.—ESTIMATION OF SCANDIUM IN PRESENCE OF IRON AND MANGANESE

Sc_2O_3 taken, *mg*	Fe_2O_3 added, *g*	MnO added, *g*	Sc_2O_3 found, *mg*	% Error
100	2·0	—	101·0	+1·0
100	4·0	—	98·8	−1·2
50	2·0	—	48·6	−2·8
50	4·0	—	48·8	−2·4
50	6·0	—	48·4	−3·2
100	—	1·26	100·4	+0·4
50	—	0·63	49·7	−0·6
50	—	1·26	48·8	−2·4
50	—	1·89	48·6	−2·8
50	4·0	0·63	48·2	−3·6
30	4·0	0·63	28·6	−4·6
20	4·0	0·63	18·8	−6·0

Total volume of solutions: 100 ml.

Determination of scandium in wolframite and ore-residues

Mix about 100 g* of the finely ground ore (−200 mesh) intimately with 50 g of anhydrous sodium carbonate, 15 g of sodium nitrate and 10 g of sodium chloride and heat the mixture to 500–550° for 1 hr in a mild steel crucible. (These are the optimum conditions for the extraction of tungsten from wolframite.[8]) Digest the cooled mass with 300 ml of water for about 30 min and filter. Wash the residue thrice with 100 ml of hot water by decantation. Digest the residue with 200 ml of conc. hydrochloric acid for about an hour on a hot-plate, and then filter. Bring the volume of the solution to 200 ml by addition of conc. hydrochloric acid (to replace acid lost during the digestion and make the final acidity of the solution about 8*M*). Extract the scandium with TBP and estimate it as oxide by the procedure described above. In the case of ore-residues obtained after the extraction of tungsten, the same procedure is adopted after direct treatment of the residue with conc. hydrochloric acid.

In a typical analysis of a sample of wolframite obtained from Rajasthan, India, 30 mg of scandium oxide were obtained from 100 g of the ore, corresponding to a scandium content of 0·030%. The same sample gave a scandium content of 0·028% on analysis by the method of Schoeller and Powell.

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Summary—The separation of scandium from iron and manganese by extraction with TBP from hydrochloric acid was studied in detail and this method was applied to the estimation of scandium in wolframite and its residues. The method consists of the extraction of tungsten from the wolframite with sodium carbonate, dissolution of the residue in hydrochloric acid and preferential extraction of iron and scandium from hydrochloric acid, stripping of the scandium with 8 *M* hydrochloric acid and re-extraction of accompanying iron with fresh TBP, precipitation of scandium with ammonia in presence of ammonium chloride, and final purification of the scandium by TBP extraction.

* The amount of the ore to be taken depends on its scandium content. The error will be more than 6% if the total scandium content of the sample used is less than 25 mg.

Résumé—On a étudié en détail la séparation du scandium du fer et du manganèse par extraction au TBP à partir d'acide chlorhydrique, et cette méthode a été appliquée à l'estimation du scandium dans la wolframite et ses résidus. La méthode consiste en l'extraction du tungstène de la wolframite par le carbonate de sodium, la dissolution du résidu en acide chlorhydrique et l'extraction préférentielle du fer et du scandium de l'acide chlorhydrique, l'élimination du scandium par l'acide chlorhydrique 8 M et la réextraction du fer qui l'accompagne par du TBP frais, la précipitation du scandium à l'ammoniaque en présence de chlorure d'ammonium et la purification finale du scandium par extraction au TBP.

Zusammenfassung—Die Abtrennung von Scandium von Eisen und Mangan durch Extraktion mit TBP aus salzsaurem Medium wurde im Detail untersucht und die Methode zur Bestimmung von Scandium in Wolframit und seinen Rückständen angewandt. Die Methode besteht aus der Extraktion von Wolfram aus dem Wolframit mit Natriumcarbonat, Auflösen des Rückstandes in Salzsäure und bevorzugte Extraktion von Eisen und Scandium aus der Salzsäure, Rückextraktion des Scandiums mit 8 M Salzsäure und Rückextraktion des begleitenden Eisens mit frischem TBP, Fällung von Scandium mit Ammoniak in Gegenwart von Ammonchlorid und schließlich Reinigung des Scandiums durch TBP-Extraktion.

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PRELIMINARY COMMUNICATIONS

Precipitation from homogeneous solution by photochemical action. Determination of thorium

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ALTHOUGH precipitation from homogeneous solution is a well established method in analytical chemistry, the application of a photochemical reaction to produce the precipitating reagent and yield quantitative results is novel. Yen and Yang[1] reported a method for the precipition of tantalum selenite from homogeneous solution which was based on the indirect catalytic destruction of the masking ion, oxalate, by photochemically produced bromine. Their method was not quantitative nor did it involve the direct production of the precipitating ion by photochemical action.

The advantages of photochemical methods lie in the temperature-independent control of the experimental parameters (light intensity, time of exposure, nature of the radiation). In principle, any absorbing substance or ion which can be reduced or oxidized photochemically is potentially useful for photochemical precipitation methods. In practice, the wavelength region in which such photochemical redox reactions usually take place is the ultraviolet where radiation sources are readily available. Therefore, other absorbers of ultraviolet radiation should be absent so that the radiation is absorbed primarily by the ion or substance undergoing the desired photochemical change.

Thorium iodate has been precipitated from homogeneous solution by Stine and Gordon[2] who reduced periodate chemically by reaction with ethyleneglycol acetate (2-hydroxyethyl acetate). The photochemical reduction of periodate to iodate has been described by Head.[3,4] Aqueous solutions of metaperiodate show an absorption band in the ultraviolet with a maximum at 2200 Å ($\varepsilon = 9{\cdot}8 \times 10^3$ l. mole^{-1} cm^{-1}) and an absorptivity of $1{\cdot}8 \times 10^3$ l. mole^{-1} cm^{-1} at 2537 Å.

Previous methods for the precipitation of thorium iodate, such as that of Meyer and Speter,[5] made use of dilute nitric acid solution. In the photochemical method, the presence of nitrate is undesirable because of its ultraviolet absorption, and perchloric acid should therefore be used.

EXPERIMENTAL

A low-pressure mercury resonance lamp with a quartz envelope (Nester Faust Co.) was used. Approximately 85–90% of the output of the lamp is at 2537 Å.

Reagent grade thorium nitrate monohydrate was dissolved in water and heated with a slight excess of reagent grade perchloric acid (70–72%) until fumes of perchloric acid appeared. The mass was cooled, more perchloric acid was added, and the fuming was repeated. The residue was dissolved in water and diluted to yield a solution containing approximately 1·6 g of perchloric acid per 100 ml of solution. Thorium was determined by the method given by Vogel,[6] but with the following more specific conditions: a solution containing about 100 mg of thorium was mixed with 225 ml of water and 5 ml of conc. hydrochloric acid and heated to boiling. Hot 10% oxalic acid dihydrate solution (55 ml) was added slowly with constant stirring. The solution was digested for 2 hr below the boiling point, then kept at room temperature overnight. The precipitate of thorium was filtered off on medium retention ashless filter paper and washed with 150–200 ml of a solution which contained 2·5 g of oxalic acid and 3·5 ml of conc. hydrochloric acid per 100 ml. The filter paper and precipitate were dried, ashed and ignited in an electric muffle furnace at 700–800° to yield thorium dioxide.

Water (60 ml) and 60% perchloric acid (10 ml) were placed in a 10 × 5 cm crystallizing dish. Reagent grade sodium periodate (4 g) was added and the solution was stirred until the solid had dissolved. Thorium perchlorate solution containing 35–180 mg of thorium was added and the dish was placed under the ultraviolet lamp in a reproducible position. Aluminium foil covered the upper surface of the lamp in order to serve as a reflector and as protection for the operator. A 4-hr exposure was found to be adequate for these experimental conditions. The contents of the dish were transferred to a 400-ml beaker and the dish was rinsed into the beaker with 50 ml of water. The contents of the beaker were allowed to cool for 15 min and were filtered through American S and S

TABLE I

Thorium taken, *mg*	Error in thorium found, *mg*			
181·4	+0·2	−0·4		
143·4	+0·1	−0·2		
144·7	−0·1	−0·3	−0·3	+0·2
107·8	+0·6	0·0	+0·1	−0·3
71·30	+0·1	+0·1	−0·1	−0·1
34·75*	+0·1	0·0	0·0	0·0

* 12-hr digestion.

No. 589 blue label filter paper (high retentivity). The precipitate was dissolved off the filter paper with 100 ml of 1*M* hydrochloric acid and the same solution was used for dissolving any precipitate adhering to the crystallizing dish. The iodate was reduced to iodide by adding solid sodium sulphite (reagent grade) until the iodine colour was discharged. The solution was heated to 60–70° and filtered ammonia solution was added until the solution contained a slight excess. The resulting thorium hydroxide was filtered off on American S and S No. 589 white label filter paper (medium retentivity) and washed with water until the excess of ammonia was removed. The precipitate was dissolved in 150 ml 0·5*M* hydrochloric acid and the solution was collected in a 600-ml beaker. The solution was diluted to approximately 250 ml and the thorium was determined by the oxalate procedure given above.

RESULTS AND DISCUSSION

Results are summarized in Table I. The over-all standard deviation (20 results) was 0·2 mg. The precipitates obtained by this method were dense and crystalline. In contrast, voluminous and very gelatinous precipitates are obtained by the direct precipitation of thorium by iodate. The volume of precipitate, after settling, was only about a tenth of that obtained by the conventional method. Photomicrographs of the precipitates obtained by these two methods also indicate a pronounced difference in the density of the precipitates.

The final determination of thorium by the oxalate method was adopted with a view to separating thorium from zirconium, iron and titanium, which frequently accompany thorium in its ores and which are also precipitated as the iodates. With small amounts of thorium longer digestion periods were required for complete precipitation of thorium oxalate.

The amount of sodium periodate required by this method is much lower than that required in the method of Stine and Gordon.[3] Furthermore, that procedure cannot be regarded as pure precipitation from homogeneous solution because of the necessity of adding 2 g of potassium iodate at the end for complete precipitation of the thorium iodate.

When attempts were made to carry out the final determination by precipitating thorium hydroxide and igniting it to thorium dioxide, high results were obtained, probably because of coprecipitation of the sodium salts present. In addition, the ignited residues were slightly brownish in colour, indicating the presence of an impurity.

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Summary—Thorium was precipitated from homogeneous solution by photochemical reduction of periodate to iodate in a solution containing thorium and perchloric acid, by means of a 2537 Å low-pressure mercury vapour lamp. For weighing, the precipitate was redissolved, precipitated once as thorium hydroxide, and finally as thorium oxalate, which was ignited to thorium dioxide. Quantitative results were obtained in the range 35–180 mg of thorium.

Résumé—On a précipité le thorium d'une solution homogène par réduction photochimique du periodate en iodate dans une solution contenant du thorium et de l'acide perchlorique, au moyen d'une lampe à vapeur de mercure à basse tension à 2537 Å. Pour la pesée, le

précipité est redissous, précipité une fois à l'état d'hydroxyde de thorium, et finalement à l'état d'oxalate de thorium qui est calciné en bioxyde de thorium. On a obtenu des résultats quantitatifs dans le domaine allant de 35 à 180 mg de thorium.

Zusammenfassung—Thorium wurde aus homogener, Thorium und Überchlorsäure enthaltender Lösung gefällt durch photochemische Reduktion von Perjodat zu Jodat bei 2537 Å mit Hilfe einer Niederdruck-Quecksilberdampflampe. Zum Auswiegen wurde der Niederschlag wieder gelöst, einmal als Thoriumhydroxyd und zuletzt als Thoriumoxalat gefällt; dieses wurde zu Thoriumdioxyd verglüht. Quantitative Ergebnisse wurden im Bereich 35–180 mg Thorium erzielt.

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Neutron absorptiometric titration

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MEINKE[1] studied the possibility of utilizing the absorption of neutrons for the determination of non-absorbing elements (which have an insignificant thermal neutron cross-section) and called the technique "indirect neutron absorptiometry".

We propose to use this principle in titrimetric analysis for the determination of the end-point ("neutron absorptiometric titration"). In this titration the effective component of the titrant (or of the solution titrated) must contain an element with a large absorption cross-section for thermal neutrons, and the titration products must be separable from the initial components as another phase (precipitation or dissolution; extraction into a non-miscible solvent and so on). For instance, in titrations based on precipitate formation, measurement is made of the absorption of thermal neutrons in the liquid separated from the precipitate. If the titrant contains an element with a large thermal neutron absorption cross-section (*e.g.*, cadmium) the measured value of the neutron absorption up to the end-point will be insignificant, because the added effective component is bound in the precipitate and the neutron absorption measurements are made on the liquid residue but will increase after the end-point is reached, as excess of the neutron-absorbing titrant is added. The end-point can easily be determined graphically.

This titration can be carried out both in a discontinuous or in a continuous (automatic) manner. The liquid sample is placed between the neutron-source and the neutron-detector.

Three methods of titration can be applied.[2]

Filtration method. After the addition of a certain amount of titrant, the supernatant liquid is filtered by suction into the measuring cuvette, which is placed between the neutron source and the neutron detector, and the neutron radiation is measured. This liquid is returned to the bulk solution, another portion of titrant is added, and the whole process is repeated. The time required for the titration is 30–40 min.

Centrifugation method. Identical amounts of the test solution are transferred into several centrifuge tubes, various amounts of the titrant are added, and the solutions are then diluted to the same volume with distilled water. The precipitate formed is then sedimented by centrifuging. The absorption of neutrons in the supernatant liquids is measured in the measuring cuvette. The time required for the titration is about 25 min.

précipité est redissous, précipité une fois à l'état d'hydroxyde de thorium, et finalement à l'état d'oxalate de thorium qui est calciné en bioxyde de thorium. On a obtenu des résultats quantitatifs dans le domaine allant de 35 à 180 mg de thorium.

Zusammenfassung—Thorium wurde aus homogener, Thorium und Überchlorsäure enthaltender Lösung gefällt durch photochemische Reduktion von Perjodat zu Jodat bei 2537 Å mit Hilfe einer Niederdruck-Quecksilberdampflampe. Zum Auswiegen wurde der Niederschlag wieder gelöst, einmal als Thoriumhydroxyd und zuletzt als Thoriumoxalat gefällt; dieses wurde zu Thoriumdioxyd verglüht. Quantitative Ergebnisse wurden im Bereich 35–180 mg Thorium erzielt.

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Three methods of titration can be applied.[2]

Filtration method. After the addition of a certain amount of titrant, the supernatant liquid is filtered by suction into the measuring cuvette, which is placed between the neutron source and the neutron detector, and the neutron radiation is measured. This liquid is returned to the bulk solution, another portion of titrant is added, and the whole process is repeated. The time required for the titration is 30–40 min.

Centrifugation method. Identical amounts of the test solution are transferred into several centrifuge tubes, various amounts of the titrant are added, and the solutions are then diluted to the same volume with distilled water. The precipitate formed is then sedimented by centrifuging. The absorption of neutrons in the supernatant liquids is measured in the measuring cuvette. The time required for the titration is about 25 min.

Automatic titration. The titrant is added to the test solution at a steady rate, and a precipitate is formed. The supernatant liquid is pumped through a filter plate in the titration flask, into the measuring cuvette, and back again into the titration flask, by a laboratory micro-pump. The neutron-detector is attached to a rate-meter and the count rate indicated is continuously registered by an appropriate recording device. The automatic apparatus reduces the time required for the titration to 5–8 min.[8]

Preliminary experiments have been carried out with a plutonium-beryllium source ($5{\cdot}5 \times 10^6$ n/sec) and a neutron scintillation detector. In our first experiments sulphide ions were titrated with 1*M* cadmium nitrate by the centrifugation method. The ratio C_1/C_2, where C_1 and C_2 are the respective neutron count rates for water and supernatant liquid in the cuvette, was plotted against volume of titrant added. The end-point was indicated by the break in the titration curve. In such a way 48 mg of sulphide were determined with an error of $\pm 0{\cdot}5$ mg.

The sensitivity and accuracy of the determination depend on the geometry of the measurement system, on the neutron flux, and on the properties of the neutron detector.

Further experiments are being done on titrations based on precipitate formation, the titrants being cadmium nitrate ($\sigma_{Cd} = 2550$ barns) for determination of fluoride, sulphide and oxalate; sodium tetraphenylborate ($\sigma_B = 750$ barns) for determination of thallium, potassium, rubidium and caesium; and potassium iodomercurate ($\sigma_{Hg} = 380$ barns) for determination of alkaloids (σ is the neutron absorption cross-section of the species indicated by subscript).

The titration method based on absorption of neutron radiation offers the advantage over the methods of radiometric titration applied so far, of using a sealed source of radiation, and is thus less hazardous. Neutron absorptiometric titration also extends the field of applicability of neutron-absorptiometric determinations.

Preliminary results indicate that the idea of neutron absorptiometric titration has considerable potential for the determination of many elements.

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Summary—A method is outlined for detection of two-phase titration end-points by means of an abrupt change in the neutron-absorption characteristics of one of the phases. One of the components of the precipitate must have a large neutron absorption cross-section, and the disappearance or appearance of neutron absorption by the supernatant liquid from the precipitation reaction then marks the completion of precipitation.

Résumé—On donne un aperçu d'une méthode pour la détection des points de fin de titrage dans les dosages à deux phases au moyen d'un changement brusque des caractéristiques de l'absorption neutronique de l'une des phases. L'un des composants du précipité doit avoir un important profil d'absorption neutronique et la disparition ou l'apparition de l'absorption neutronique par le liquide surnageant de la réaction de précipitation marque alors la fin de la précipitation.

Zusammenfassung—Es wird eine Methode zur Endpunktsbestimmung in Zweiphasentitrationen durch jähen Wechsel in der Neutronenabsorptionscharakteristik einer der Phasen skizziert. Eine der Komponenten des Niederschlags muß einen großen Neutronenabsorptionsquerschnitt haben; Verschwinden oder Auftreten von Neutronenabsorption in der Flüssigkeit über dem Niederschlag zeigt dann das Ende der Fällung an.

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KINETICS AND MECHANISM OF THE REACTION BETWEEN BIACETYL AND HYDROXYLAMINE IN ACID SOLUTION

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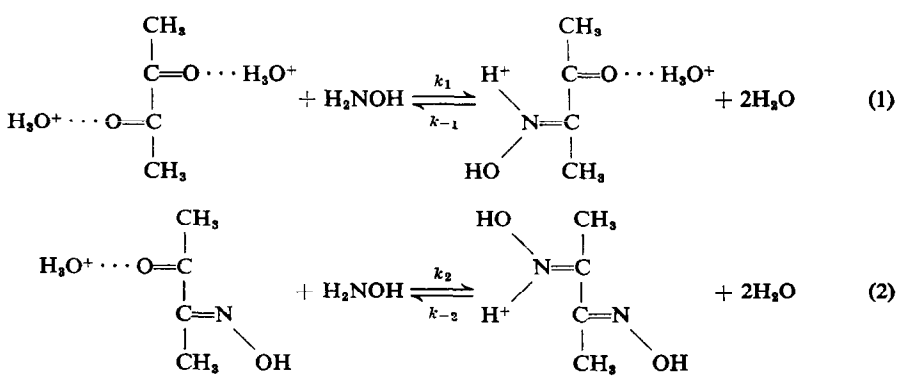
Summary—The kinetics and mechanism of formation of dimethylglyoxime from biacetyl and hydroxylamine in acid solution have been studied. Unprotonated hydroxylamine was found to react with the hydrogen-bonded carbonyl group to give the conjugate acid of the oxime. Detectable quantities of carbinolamine intermediates were not found in the acid concentration range studied.

THE kinetics and mechanism of oxime, semi-carbazone and, in general, Schiff's base formation have been the subject of many investigations. A comprehensive series of papers on Schiff's base formation was initiated in 1959 by Jencks[1] who studied the kinetics and mechanism involved over a wide acid concentration range. The variation in rate-determining steps in the reaction sequence explained many of the previous inconsistent results.

Hileman and Gordon[2] studied the kinetics and mechanism of the reaction of biacetyl and hydroxylamine at pH 7·0. Their results showed that this system generated dimethylglyoxime in accordance with the model proposed by Cordes and Jencks[3] for this pH.

The present investigation is concerned with the kinetics and mechanism of the reaction of biacetyl and hydroxylamine in hydrochloric acid solution. On the basis of the Jencks model the expected sequence for the reaction of biacetyl with hydroxylamine in acid solution should be:



Free hydroxylamine should react reversibly with the hydrogen-bonded carbonyl group to give the conjugate acid of the Schiff's base. Hileman and Gordon[2] showed that in neutral solution the decomposition of a carbinolamine intermediate is the

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rate-determining step; because of acid catalysis, the decomposition of this intermediate should be very fast in acid solution, and its concentration very small.

EXPERIMENTAL

Apparatus

All spectrophotometric measurements were carried out on a Cary model No. 14 recording spectrophotometer equipped with a thermostatic cell compartment (±0·05°).

Chemicals

Hydroxylamine hydrochloride (Baker analysed reagent) was purified by recrystallization from 95% ethanol. After filtration the residual ethanol was removed by air-drying with an aspirator. Water was removed by drying over calcium chloride in a desiccator. The purified hydroxylamine hydrochloride was found to be 99·9% pure by indirect titration.[4]

Biacetyl monoxime (Matheson, Coleman and Bell) was triply sublimed at 35° and approximately 1 mm Hg pressure.

PFHS-grade biacetyl obtained from Burdick and Jackson Laboratories, Muskegon, Michigan, was used without further purification.

Dimethylglyoxime (Baker analysed) was dried in a desiccator over calcium chloride and also used without further purification.

Procedure for kinetic studies

A spectrophotometric cell containing a solution of hydrochloric acid and all the other reagents except one was brought to constant temperature. Then 0·04807 ml of a solution of the last reagent necessary to start the reaction was added from a Hamilton microlitre syringe. The absorbance was measured at a set wavelength at various times after the addition of the last reagent.

THEORY

HD = dimethylglyoxime
HDH^+ = protonated dimethylglyoxime
HM = biacetyl monoxime
HMH^+ = protonated biacetyl monoxime
Hx = hydroxylamine
HxH^+ = protonated hydroxylamine
B = biacetyl
$B(OH)_2$ = hydrated biacetyl

The hydration constant K_h, for biacetyl is given by

$$K_h = \frac{a_{B(OH)_2}}{a_B}. \tag{3}$$

Mass balance shows that

$$[Y]_T = [Y] + [YH^+] \tag{4}$$

where $[Y]_T$ is the total concentration of the various Y species and Y = HD, HM or Hx; $YH^+ = HDH^+$, HMH^+ or HxH^+. Similarly

$$[B]_T = [B] + [B(OH)_2]. \tag{5}$$

The apparent equilibrium constants for equations (1) and (2) are

$$K_1' = \frac{[HM]_T}{[B]_T[Hx]_T} = \frac{k_1'}{k_{-1}'} \tag{6}$$

$$K_2' = \frac{[HD]_T}{[HM]_T[Hx]_T} = \frac{k_2'}{k_{-2}'} \tag{7}$$

$$[B] = \frac{A^{4065}}{\varepsilon_B^{4065}} \tag{8}$$

where A^{4065} denotes the absorbance of B at 4065 Å and ε_B^{4065} its molar absorbtivity; only biacetyl absorbs in the visible.

The absorbance A is given by

$$A = \varepsilon_{HM}[HM] + \varepsilon_{HD}[HD]_T \tag{9}$$

where the ε values are the molar absorptivities of the species indicated by the subscripts.

$$[HM]_i = [HM] + [HD]_T \tag{10}$$

where the subscript i denotes the initial value.

Similarly

$$[Hx]_T = [Hx]_i - [HM] \tag{11}$$

$$[HM] = \frac{A_{HM}}{\varepsilon_{HM}^{2275}}. \tag{12}$$

The acid dissociation constant is given by

$$K_A^Y = h_0 \frac{[Y]}{[YH^+]} \tag{13}$$

where Y = HD, HM or Hx; correspondingly $YH^+ = HDH^+$, HMH^+ or HxH^+.

$$A = \varepsilon_{HD}[HD] + \varepsilon_{HDH^+}[HDH^+] \tag{14}$$

$$[HD]_i = [HD] + [HDH^+]. \tag{15}$$

The thermodynamic equilibrium constants for equations (1) and (2) are

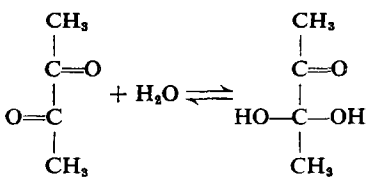
$$K_1 = \frac{a_{HMH^+}}{a_B a_{Hx} a_{H^+}} \tag{16}$$

$$K_2 = \frac{a_{HDH^+}}{a_{HM} a_{Hx} a_{H^+}} \tag{17}$$

RESULTS

Hydration

It is known that biacetyl is hydrated[5,6,7] in aqueous solution:



(18)

The method employed here to determine the extent of hydration is that described by Bell and McDougall.[6] The extinction coefficient of the visible band for biacetyl

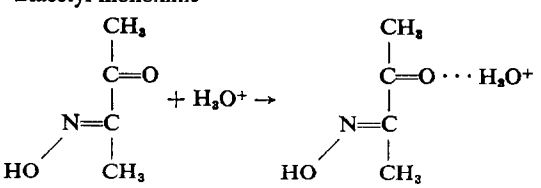
employed in this study is 20·3. This is the average of the extinction coefficients of the visible band found by Foster[8] in a series of non-aqueous polar solvents.

As shown in Fig. 1, plotting the extinction coefficient of the visible peak for biacetyl versus 1/[HCl] and extrapolating to infinite hydrochloric acid concentration (where the water concentration is zero and hydration cannot occur) results in a value

TABLE I.—HYDRATION CONSTANTS FOR BIACETYL AT 25·0°C

[HCl], M	$K_h \frac{f_B}{f_{B(OH)_2}}$ [KCl] = 0	[KCl] = 2M
0·812	2·35	2·19
0·609	2·42	2·52
0·406	2·52	2·58
0·203	2·62	2·87
0·101	2·68	2·99

Biacetyl monoxime*



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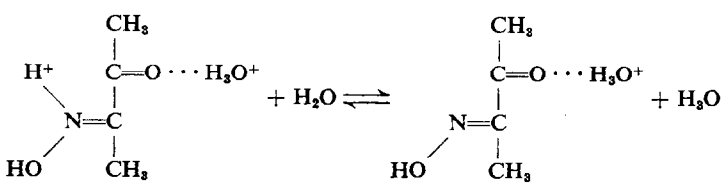

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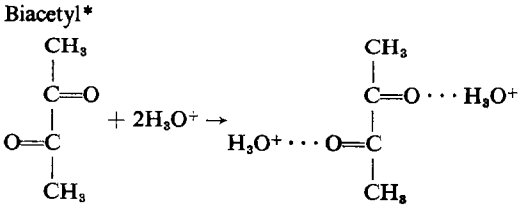
Biacetyl*



(23)

The acid dissociation constants of the conjugate acids of biacetyl monoxime and dimethylglyoxime, determined by Ellefsen and Gordon,[9] show that at concentrations of hydrochloric acid below about 1M, the extent of protonation of biacetyl monoxime is very small. However, the extent of protonation of dimethylglyoxime in 0·101–0·812M hydrochloric acid is significant. Therefore, in order to simplify determination of the concentration of dimethylglyoxime, absorbance measurements used in determining the kinetics for dimethylglyoxime were carried out at 2376 Å, the isosbestic point for dimethylglyoxime (*cf.* Ellefsen and Gordon[9] for the ultraviolet spectra of HD, HDH^+, HM, and HMH^+).

Rate and equilibrium constants

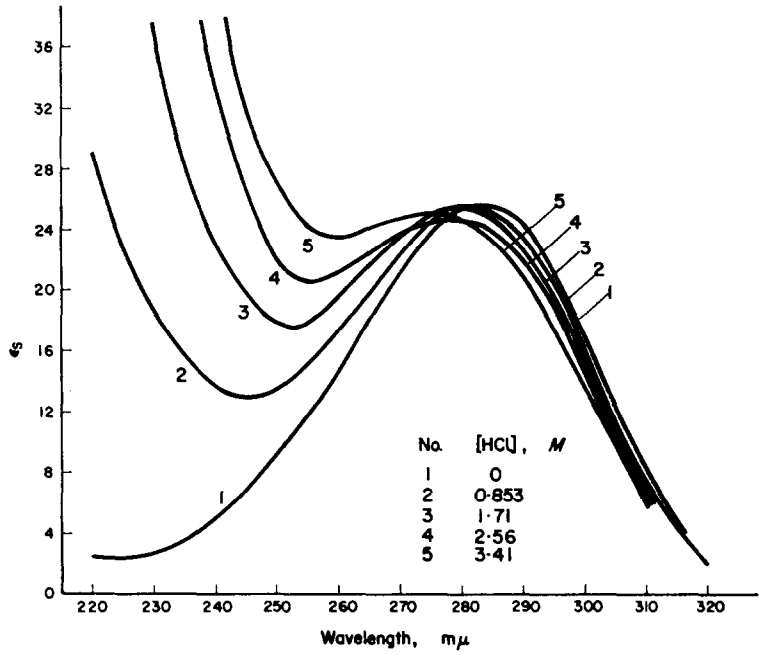


FIG. 2.—The effect of hydrochloric acid concentration on the ultraviolet absorption spectrum of biacetyl.

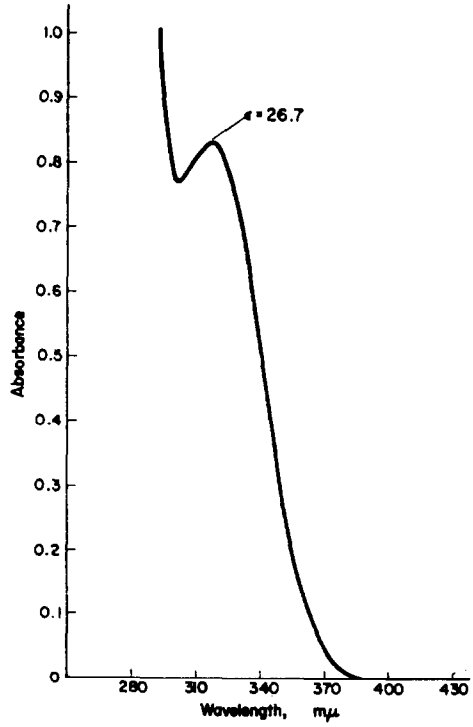


FIG. 3.—The ultraviolet absorption spectrum of biacetyl monoxime in dioxane.

TABLE I.—HYDRATION CONSTANTS FOR BIACETYL AT 25·0°C

	$K_h \frac{f_B}{f_{B(OH)_2}}$	
[HCl], M	[KCl] = 0	[KCl] = 2M
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0·101	2·68	2·99

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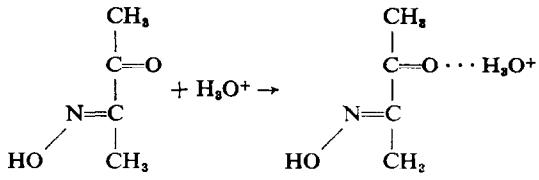

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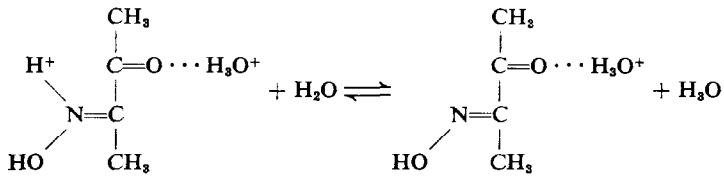

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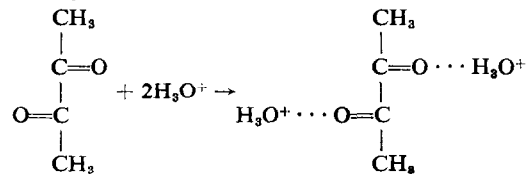
Biacetyl*



(23)

The acid dissociation constants of the conjugate acids of biacetyl monoxime and dimethylglyoxime, determined by Ellefsen and Gordon,[9] show that at concentrations of hydrochloric acid below about 1M, the extent of protonation of biacetyl monoxime is very small. However, the extent of protonation of dimethylglyoxime in 0·101–0·812M hydrochloric acid is significant. Therefore, in order to simplify determination of the concentration of dimethylglyoxime, absorbance measurements used in determining the kinetics for dimethylglyoxime were carried out at 2376 Å, the isosbestic point for dimethylglyoxime (*cf.* Ellefsen and Gordon[9] for the ultraviolet spectra of HD, HDH^+, HM, and HMH^+).

Rate and equilibrium constants

All rate and equilibrium constants were first calculated from values of HD_T, HM_T, Hx_T, and B_T as indicated in equations (4)–(7). The trends observed in these constants as the acid concentration is varied are used to determine the reaction mechanism. A preliminary value of K_1' at 25·0° and in 0·406M HCl was obtained by spectrophotometrically following first the decomposition of dimethylglyoxime, and

* These reactions are considered to be essentially irreversible.

second, the decomposition of biacetyl monoxime until equilibrium had been obtained.

From measurements of the absorbance at 4065 Å and 2550 Å, the concentrations of biacetyl, hydroxylamine, biacetyl monoxime and dimethylglyxoime were calculated from equation (8) and the equations below;[10] no detectable quantities of carbinolamine intermediates were found to be present:

$$A^{2550} = \varepsilon_{HM}[HM] + \varepsilon[HD]_T$$

where ε is the extinction coefficient of the mixture of HD and HDH^+ in 0·406M hydrochloric acid and is constant at constant acid concentration,

$$[B] + [HM] + [HD]_T = [B]_i + [HM]_i + [HD]_i = \text{known constant}$$

$$[Hx]_T + [HM] + 2[HD]_T = [Hx]_i + [HM]_i + 2[HD]_i = \text{known constant.}$$

It was found that at equilibrium only biacetyl, hydroxylamine and biacetyl monoxime remained in solution in detectable quantities; the calculations indicated the absence of dimethylglyoxime in both cases. The preliminary values of K_1' were calculated to be $3{\cdot}9 \times 10^3$ and $3{\cdot}5 \times 10^3$ l. mole^{-1} respectively.

Determination of the equilibrium and rate constants K_2', k_2' and k_{-2}' was carried out by treating excess of hydroxylamine with biacetyl monoxime under conditions such that the formation of dimethylglyoxime took place by a pseudo first-order reversible reaction sequence. The reaction was followed at 2376 Å and the conditions employed are shown in Table II; measurements were also carried out in 2·00M

TABLE II.—K_2', k_2' AND k_{-2}' AS A FUNCTION OF ACID CONCENTRATION AT 25·0°C

[HCl], M	$[Hx]_i$, M	[KCl], M	K_2' l. mole^{-1}	$k_2' \times 10^2$ l. mole^{-1} . min^{-1}	$k_{-2}' \times 10^2$ min^{-1}
0·812	0·4339	0·00	2·22 ± 0·04	8·63 ± 0·36	3·90 ± 0·05
0·609	0·3841	0·00	2·81 ± 0·18	9·52 ± 0·65	3·38 ± 0·03
0·406	0·2876	0·00	4·71 ± 0·16	11·3 ± 0·5	2·39 ± 0·05
0·203	0·1476	0·00	9·50 ± 0·08	13·4 ± 0·5	1·41 ± 0·04
0·101	0·1079	0·00	17·6 ± 0·4	15·1 ± 0·4	0·860 ± 0·033
0·812	0·9146	2·00	1·08 ± 0·01	6·75 ± 0·16	6·28 ± 0·14
0·609	0·7062	2·00	1·41 ± 0·01	7·75 ± 0·17	5·50 ± 0·09
0·406	0·5998	2·00	2·12 ± 0·04	9·54 ± 0·16	4·50 ± 0·06
0·203	0·2995	2·00	4·71 ± 0·29	12·9 ± 1·2	2·74 ± 0·10
0·101	0·2158	2·00	8·80 ± 0·39	13·9 ± 0·4	1·58 ± 0·05

In all determinations, $[HM]_i = 2{\cdot}100 \times 10^{-4}M$. All the results shown are the average of three determinations.

potassium chloride to correspond with a concomitant study involving the precipitation of palladium dimethylglyoximate. Under the conditions used, the decomposition of biacetyl monoxime into biacetyl and hydroxylamine was negligible. The absorbance was measured at intervals of time until equilibrium was obtained. The concentrations of biacetyl monoxime and dimethylglyoxime at various times as well as at equilibrium were calculated from equations (9) and (10), and the equilibrium and rate constants were calculated from a reversible first-order rate equation. The results are also shown in Table II.

The determination of the equilibrium and rate constants K_1', k_1' and k_{-1}' was carried out by letting $6{\cdot}696 \times 10^{-6}M$ hydroxylamine react with $3{\cdot}566 \times 10^{-4}M$ biacetyl. Under these conditions, practically no dimethylglyoxime is formed and the

formation of biacetyl monoxime takes place by a pseudo first-order reversible reaction. The formation of biacetyl monoxime was followed at 2275 Å. The constants K_1', k_1' and k_{-1}' were calculated from a first-order reversible rate law and equations (11) and (12). The results of these determinations are shown in Table III.

Several independent checks were made on the magnitude of the equilibrium and rate constants determined by these methods. For example, it was found that the decomposition of dimethylglyoxime in 0·406*M* hydrochloric acid at 25·0° takes place by an irreversible first-order rate law. The rate constant k_{-2}' was found to be 0·0234 min^{-1}. This compares favorably with 0·0239 min^{-1} determined by the previous procedure (*cf.* Table II).

Values of K_1', k_1' and k_{-1}' were also obtained by following the decomposition of biacetyl monoxime at 2275 Å in 0·406*M* hydrochloric acid at 25·0°. The equilibrium and rate constants were calculated from first- and second-order reversible rate laws. Values of K_1', k_1' and k_{-1}' calculated by this method are $5{\cdot}27 \times 10^3$ l. $mole^{-1}$, 10·3 l. $mole^{-1}$. min^{-1} and $1{\cdot}96 \times 10^{-3}$ min^{-1} respectively. The values obtained by the previous procedure were $4{\cdot}65 \times 10^3$ l. $mole^{-1}$, 9·39 l. $mole^{-1}$. min^{-1} and $2{\cdot}04 \times 10^{-3}$ min^{-1} (*cf.* Table III).

TABLE III.—K_1', k_1' AND k_{-1}' AT 25·0°C AS A FUNCTION OF ACID CONCENTRATION

[HCl], *M*	$K_1' \times 10^{-3}$, *l. mole*$^{-1}$	k_1', *l. mole*$^{-1}$. *min*$^{-1}$	$k_{-1}' \times 10^3$, *min*$^{-1}$
		[KCl] = 0	
0·812	2·23 ± 0·12	7·85 ± 0·25	3·53 ± 0·09
0·609	2·91 ± 0·02	8·29 ± 0·15	2·91 ± 0·06
0·406	4·65 ± 0·06	9·38 ± 0·15	2·04 ± 0·01
0·203	9·17 ± 0·44	11·2 ± 0·4	1·24 ± 0·05
0·101	15·3 ± 0·8	13.3 ± 0·1	0·869 ± 0·038
		[KCl] = 2·00*M*	
0·812	1·08 ± 0·04	6·49 ± 0·47	5·94 ± 0·49
0·609	1·52 ± 0·04	7·47 ± 0·08	4·97 ± 0·19
0·406	2·18 ± 0·06	7·61 ± 0·19	3·53 ± 0·04
0·203	4·75 ± 0·01	9·92 ± 0·13	2·11 ± 0·02
0·101	9·44 ± 0·17	12·1 ± 0·00	1·29 ± 0·02

All the results shown are the average of three determinations.

It was found that the values of the rate and equilibrium constants for the reaction of biacetyl with hydroxylamine and the reaction of biacetyl monoxime with hydroxylamine were unchanged upon determination at a different wavelength; change in the initial concentrations of reactants had no effect on the rate or equilibrium constants in any of the methods.

Acidity functions

In the ensuing discussion, acidity functions[11] play a role, so values of the acidity functions were determined for the solutions in which equilibrium and rate constants were measured. Dimethylglyoxime was used as an indicator.

The absorbance at 2550 Å of an equilibrium mixture of undecomposed protonated and unprotonated dimethylglyoxime (obtained by extrapolation of the decomposition back to zero time) was measured in each of the solutions represented in columns 3, 4 and 5 of Table IV. This value and equations (13), (14) and (15) were then used to

calculate h_0. The results are shown in Table IV. For the solutions used in the determination of K_1', k_1' and k_{-1}', the effect of the hydroxylamine and biacetyl on the acidity function can be neglected because of their low concentrations; thus, the values shown in the second column of Table IV were taken directly from the literature.[11]

TABLE IV.—THE ACIDITY FUNCTIONS

[HCl], M	h_0			
	a		b	
	[KCl] = 0	[KCl] = 2M	[KCl] = 0	[KCl] = 2M
0·812	1·18	1·30	2·18	3·37
0·609	0·804	0·772	1·60	2·11
0·406	0·483	0·535	0·988	1·24
0·203	0·234	0·259	0·499	0·553
0·101	0·113	0·149	0·235	0·300

$a = h_0$ values for the solutions used for calculation of K_1, k_1 and k_{-1}.
$b = h_0$ values for the solutions used for calculation of K_2, k_2 and k_{-2}.
$h_0 = \frac{f_B a_{H^+}}{f_{BH^+}}$ where f_{BH^+} and f_B = activity coefficients of the bases BH^+ and B.

DISCUSSION

Enolization of biacetyl

The enol content of biacetyl in aqueous solution has been measured by Schwarzenbach and Witwer.[12] They found that the enol content was $5{\cdot}6 \times 10^{-3}$ %; this enolization is therefore neglected in this study.

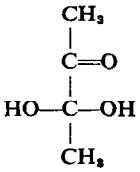
Enolization of biacetyl monoxime

As shown in Fig. 3, the extinction coefficient of the carbonyl absorption-peak of biacetyl monoxime dissolved in dioxane is 26·7. This value is approximately that which would be expected for the n-π^* transition of a carbonyl group and indicates little if any enolization in dioxane. If there is no extensive enolization in dioxane, then there will not be any in acid aqueous solution because it is known that the extent of enolization decreases as the polarity of the solvent increases.[13,14] Therefore, the enolization of biacetyl monoxime, like that of biacetyl, has been neglected.

Hydration of biacetyl

The hydration of biacetyl has been represented as taking place on only one carbonyl group. Hydration of the second carbonyl group would not be expected because $B(OH)_2$ does not possess an electron-withdrawing group adjacent to its carbonyl group, a requirement for a "hydratable" carbonyl.[15,16]

As shown in Fig. 2, little change in the extinction coefficient of the ultraviolet band of biacetyl takes place in hydrochloric acid of various concentrations, in contrast to the visible band of biacetyl.[10] The reason is that the new carbonyl compound



will have an absorption band in the ultraviolet at approximately the same point as that for biacetyl with approximately the same extinction coefficient, but will not absorb in the visible.[17] If the second carbonyl group on biacetyl was hydrated extensively, a decrease in the intensity of the ultraviolet band for biacetyl would be expected as the solvent became more polar, as well as a decrease in the visible band. This is not observed.

Hydration of biacetyl monoxime

Only some indirect evidence is available indicating that the carbonyl group of biacetyl monoxime is not appreciably hydrated. As shown by Ellefsen and Gordon,[9] a very good isosbestic point is observed for biacetyl monoxime in 0-10*M* hydrochloric acid solution. If hydration were occurring, unprotonated and protonated hydrated biacetyl monoxime, in addition to unprotonated and protonated unhydrated biacetyl monoxime, would be present. A good isosbestic point would not be observed if this were the case, because the hydration equilibrium would be expected to shift considerably, as was the case for biacetyl. Therefore, only the two unhydrated species, HM and HMH^+, must be present to an appreciable degree.

Carbinolamine intermediates

In their study of the reaction of hydroxylamine with biacetyl at pH 7, Hileman and Gordon[2] found that carbinolamine intermediates were the predominant species during much of the reaction sequence. The Jencks model predicts that the decomposition of these intermediates is acid-catalyzed. Therefore, in strongly acid solution, their decomposition would be expected to be very fast and their concentrations should remain very small. This has been found in this study. The rate constants k_1', k_{-1}', k_2' and k_{-2}' were calculated in all cases over the entire range of the reaction sequence. It was found that "constant" rate constants were obtained from zero time to the time when equilibrium had been obtained. The isosbestic points observed by Ellefsen and Gordon for biacetyl monoxime and dimethylglyoxime show that only protonated and unprotonated oxime are present at zero time. Therefore, if carbinolamine intermediates were to form to any appreciable degree in the formation or decomposition of dimethylglyoxime or biacetyl monoxime, a change in the rate constant with time would be observed. Additional evidence for lack of appreciable quantities of carbinolamine intermediates is the fact that the same rate constants were obtained by following the reactions at different wavelengths.

Spectrophotometric work has shown that the hydration of biacetyl is very fast. The protonation of hydroxylamine, dimethylglyoxime and biacetyl monoxime will also be very fast. Therefore, the rate-determining steps in oxime formation in this study will be the attack of hydroxylamine on the carbonyl group and the rate-determining step in the decomposition will be the attack of water on the oxime.

Mechanisms for the formation or the decomposition of dimethylgyloxime and biacetyl monoxime can now be proposed by analysis of the results shown in Tables II and III. All the subsequent equations are derived in terms of acidity functions.

Mechanism for the decomposition of oxime

Consideration of the variation of the activity coefficients of positively charged, neutral and hydrogen bonded species in solutions of high ionic strengths (0·101–0·812*M* hydrochloric acid) is necessary in the following discussion. In no case,

however, are the absolute values of the activity coefficients known and, for this reason, they are incorporated in the final rate and equilibrium constants.

Upon consideration of the size and charge of the ions HxH^+, HDH^+ or HMH^+, it would be expected that the activity coefficients would decrease with increase in hydrochloric acid concentration from 0·101 to 0·812*M*. The activity coefficient of neutral species such as Hx would not be expected to change greatly with this change in ionic strength. It is not obvious whether the activity coefficient of a hydrogen bonded carbonyl group would act like that of a neutral species or a positive species. However, it is sufficient to know that it will either remain constant or decrease with the specified increase in ionic strength.

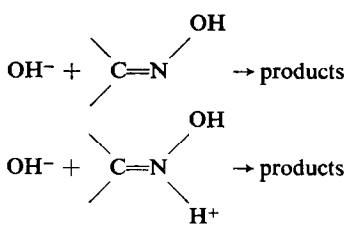
If the decomposition of dimethylglyoxime and biacetyl monoxime takes place by the attack of water on the neutral oxime molecule, the rate constants k_{-1}' and k_{-2}' would contain the activity coefficients of the neutral species HM and HD; for example, one would find for the decomposition of biacetyl monoxime that

$$\frac{-\mathrm{dHM}}{\mathrm{d}t} = k_n a_{\mathrm{HM}} \qquad (a_{\mathrm{H_2O}} \text{ is constant and included in } k_n) \tag{24}$$

or

$$\frac{-\mathrm{dHM}}{\mathrm{d}t} = k_{-1}'[\mathrm{HM}] \qquad (\text{where } k_{-1}' = k_n f_{\mathrm{HM}}). \tag{25}$$

The rate constant k_{-1}' would not be expected to change much with change in acid concentration because the activity coefficient f_{HM} would not change much. However, as seen from Table III, k_{-1}' increases rapidly with increase in acid concentration, indicating a more complicated mechanism. Likewise the following mechanisms would not be consistent with the experimental results because k_{-1}' or k_{-2}' would decrease with increase in acid concentration.



The Cordes and Jencks model[3] predicts the attack of water on the conjugate acid of the oxime. For this mechanism, the following relationships can be derived[9] from equations (4) and (13) [using HD and HDH^+ gives equation (26); using HM and HMH^+ gives equation (27)]. See equations (1) and (2) for definitions of k_{-1} and k_{-2}.

$$k_{-2}' = k_{-2} f_{\mathrm{HDH^+}} \frac{h_0}{K_{\mathrm{A}}^{\mathrm{HDH^+}} + h_0} \tag{26}$$

$$k_{-1}' = k_{-1} f_{\mathrm{HMH^+}} \frac{h_0}{K_{\mathrm{A}}^{\mathrm{HMH^+}}} \tag{27}$$

The terms $k_{-1} f_{\mathrm{HMH^+}}$ and $k_{-2} f_{\mathrm{HDH^+}}$ were calculated from the values of k_{-1}' and k_{-2}' shown in Tables II and III, the acid dissociation constants[9] and the values of h_0 shown

TABLE V.—RATE AND EQUILIBRIUM CONSTANTS FOR THE REACTION OF BIACETYL MONOXIME WITH HYDROXYLAMINE AT 25·0°C

[HCl], M	$K_2\frac{f_{HM}f_{HxH^+}}{f_{HDH^+}}$ $l.\ mole^{-1}$	$k_2 f_{HM} f_{HxH^+}$ $l.\ mole^{-1}\ .\ min^{-1}$	$k_{-2}f_{HDH^+}$ min^{-1}
	[KCl] = 0		
0·812	$4·2 \times 10^5$	$8·1 \times 10^4$	0·19
0·609	$4·1 \times 10^5$	$8·9 \times 10^4$	0·22
0·406	$4·8 \times 10^5$	$10·5 \times 10^4$	0·23
0·203	$5·0 \times 10^5$	$12·5 \times 10^4$	0·26
0·101	$4·3 \times 10^5$	$14·1 \times 10^4$	0·33
	[KCl] = 2·00M		
0·812	$2·8 \times 10^5$	$6·3 \times 10^4$	0·22
0·609	$2·6 \times 10^5$	$7·2 \times 10^4$	0·28
0·406	$2·7 \times 10^5$	$8·9 \times 10^4$	0·36
0·203	$2·6 \times 10^5$	$12·0 \times 10^4$	0·46
0·101	$2·8 \times 10^5$	$13·0 \times 10^4$	0·47

in Table IV. The results shown in column 4 of Tables V and VI show that these terms behave as predicted, *i.e.*, they decrease with increase in acid concentration. This mechanism for the decomposition of dimethylglyoxime and biacetyl monoxime also explains their stability in neutral solution where no significant protonation takes place.

Mechanism for the formation of the oxime

Protonated hydroxylamine is unreactive toward carbonyl groups[1]; further, it is also known that carbonyl groups are extremely weak bases.[18] Therefore, as pointed out by Cordes and Jencks,[3] the mechanism of formation of an oxime cannot be the attack of unprotonated hydroxylamine on a protonated carbonyl group because the rate constant for this reaction would be larger than that for a diffusion-controlled system.

If the formation of dimethylglyoxime were due to the attack of unprotonated hydroxylamine on a neutral carbonyl group, the following equation would apply to

TABLE VI.—RATE AND EQUILIBRIUM CONSTANTS FOR THE REACTION OF BIACETYL WITH HYDROXYLAMINE AT 25·0°C

[HCl], M	$K_1\frac{f_B f_{HxH^+}}{f_{HMH^+}}$ $l.\ mole^{-1}$	$k_1 f_{HxH^+} f_B$ $l.\ mole^{-1}\ .\ min^{-1}$	$k_{-1}f_{HMH^+}$ min^{-1}
	[KCl] = 0		
0·812	$5·7 \times 10^6$	$2·5 \times 10^7$	4·3
0·609	$5·1 \times 10^6$	$2·6 \times 10^7$	5·2
0·406	$5·1 \times 10^6$	$3·1 \times 10^7$	6·1
0·203	$5·0 \times 10^6$	$3·8 \times 10^7$	7·6
0·101	$4·1 \times 10^6$	$4·6 \times 10^7$	11·1
	[KCl] = 2·00M		
0·812	$2·5 \times 10^6$	$1·9 \times 10^7$	7·6
0·609	$2·6 \times 10^6$	$2·4 \times 10^7$	9·3
0·406	$2·7 \times 10^6$	$2·5 \times 10^7$	9·5
0·203	$3·1 \times 10^6$	$3·6 \times 10^7$	11·7
0·101	$3·6 \times 10^6$	$4·5 \times 10^7$	12·5

the reaction of biacetyl monoxime with hydroxylamine:

$$\frac{\mathrm{dHDH^+}}{\mathrm{d}t} = k_m a_{Hx} a_{HM} = k_2'[HM][HxH^+] \tag{28}$$

where

$$k_2' = \frac{k_m f_{Hx} f_{HM} K_A^{HxH^+}}{h_0}. \tag{29}$$

The activity coefficients f_{Hx} and f_{HM} would not be expected to change much with increase in acid concentration and therefore k_2' at a hydrochloric acid concentration of 0·101*M* would be about 10 times the value for k_2' with 0·812*M* hydrochloric acid (*cf.* Table II). This is not observed.

Campbell and Edward[18] have shown that the strength of the hydrogen bond on the carbonyl group in aliphatic ketones increases as the polarity of the solvent is increased. In the present case, the solvent polarity is increased by increase in the concentration of hydrochloric acid. It would be expected that the carbon atom in the carbonyl group would be more reactive toward hydroxylamine as the hydrogen bond became stronger. Therefore, it is assumed that the reactivity of biacetyl to hydroxylamine is proportional to $a_B a_{H^+}$ and the reactivity of biacetyl monoxime to hydroxylamine is proportional to $a_{HM} a_{H^+}$. In the reaction of biacetyl with hydroxylamine, there are two forms of biacetyl with which hydroxylamine can react. However, hydroxylamine will probably react preferentially with unhydrated biacetyl because, as shown by Cordes and Jencks,[19] a nitrogen base will react fastest with those carbonyl groups which have the more strongly electron-withdrawing groups adjacent to them.

From these relationships and equations (3) and (13) (Y and YH^+ = Hx and HxH^+), the following relationships can be derived[9]:

$$k_1' = k_1 \frac{f_B f_{HxH^+} K_A^{HxH^+}}{1 + \dfrac{K_h f_B}{f_{B(OH)_2}}} \tag{30}$$

$$k_2' = k_2 f_{HxH^+} f_{HM} K_A^{HxH^+}. \tag{31}$$

The values of k_1, k_2, $K_h f_B / f_{B(OH)_2}$ and $K_A^{HxH^+}$ are known (the value of $K_A^{HxH^+}$ used is that determined by Bissot, Parry and Campbell[20]). Therefore, the terms shown in column 3 of Tables V and VI can be obtained.

The activity coefficient of HxH^+ would be expected to decrease with increase in acid concentration and the activity coefficients of B and HM would be expected either to remain unchanged or to decrease with this change in acid concentration. If this is so, the terms in column 3 of Tables V and VI would be expected to decrease with increase in acid concentration; this is observed.

The equilibrium constants corresponding to the proposed mechanism are those shown in equations (16) and (17). The following equilibrium equations were derived for this mechanism:

$$K_1' = K_1 \frac{(f_B f_{HxH^+}) K_A^{HxH^+} K_A^{HMH^+}}{(f_{HMH^+}) h_0 \left(1 + \dfrac{K_H f_B}{f_{B(OH)_2}}\right)} \tag{32}$$

$$K_2' = K_2 \frac{(f_{HM} f_{HxH^+}) K_A^{HxH^+} (K_A^{HDH^+} + h_0)}{(f_{HDH^+}) h_0}. \tag{33}$$

By use of these equations, the terms shown in column 2 of Tables V and VI were obtained from the values of K_2' and K_1' in Tables II and III. It will be noted that in the absence and presence of potassium chloride, these terms are almost unchanged as the hydrochloric acid concentration is varied. If it is assumed that the ratio of the activity coefficient of HxH^+ to the activity coefficient of the conjugate acid of biacetyl monoxime in the term shown in column 2 of Table V and to the conjugate acid of dimethylglyoxime in the term shown in column 2 of Table VI is approximately unity for all of the acid concentrations considered, then the hydrogen bonded species HM and B must act like a neutral species, the activity coefficients remaining approximately unchanged.

It is seen that $k_{-2}f_{HDH^+}$ is smaller than $k_{-1}f_{HMH^+}$ and $k_1f_{HxH^+}f_B$ greater than $k_2f_{HxH^+}f_{HM}$ at any given acid concentration. This is attributed primarily to steric hindrance of attack by water and hydroxylamine.

Thus, with the exception of the interpretation of the nature of the reaction of hydroxylamine with the hydrogen bonded carbonyl group, the kinetics and mechanism of formation of dimethylglyoxime in acid solution are those predicted on the basis of Cordes and Jencks's model.[3]

Acknowledgement—The authors acknowledge the partial assistance of the United States Atomic Energy Commission in supporting this investigation, under Contract AT(11-1)-582.

Zusammenfassung—Kinetik und Mechanismus der Bildung von Dimethylglyoxim aus Biacetyl und Hydroxylamin in saurer Lösung wurden untersucht. Es wurde gefunden, daß nicht protoniertes Hydroxylamin mit der an einer Wasserstoffbrücke beteiligten Carbonylgruppe zur konjugierten Säure des Oxims reagiert. Im untersuchten Bereich an Säurekonzentrationen wurden keine nachweisbaren Mengen von Carbinolamin-Zwischenstufen gefunden.

Résumé—On a étudié la cinétique et le mécanisme de formation de la diméthylglyoxime à partir du diacétyle et de l'hydroxylamine en solution acide. On a trouvé que l'hydroxylamine non protonée réagit avec le groupe carbonyle à liaison hydrogène pour donner l'acide conjugué de l'oxime. On n'a pas trouvé de quantités décelables d'intermédiaires de la carbinolamine dans le domaine de concentration acide étudié.

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COMPLEXATION OF ALUMINIUM, YTTRIUM, LANTHANUM AND LANTHANIDES WITH 4-(2-PYRIDYLAZO)RESORCINOL (PAR)*

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Summary—The sensitive reactions between 4-(2-pyridylazo)resorcinol (PAR) and yttrium, lanthanum and the lanthanides can be used for the spectrophotometric determination of these elements. The method has no advantage over other methods for the determination of aluminium and lanthanum. Only M(PAR)H and M(PAR) complexes are formed in solutions where the molarity of the metal ion is greater than or nearly equal to the molarity of the ligand at pH $< 7{\cdot}5$. If there is molar excess of PAR, 1:2 complexes may be formed but this is certain only for the yttrium-PAR system. Errors in analysis may result from the simultaneous occurrence of optically different complexes; close control of pH and reagent concentration is essential. Optical and equilibrium data are given for the systems investigated.

4-(2-PYRIDYLAZO)RESORCINOL (PAR) is used as a metal-ion indicator, with ions of the elements of group IIIA of the periodic system and with aluminium, to give intensely red soluble complexes in slightly acidic medium. The sensitivity of the reactions, with the exception of that with aluminium, is high, as is shown by the values of pD at pH 6·4–6·6: scandium 7·4, yttrium 6·6, lanthanum 6·0, cerium 7·3, praseodymium 6·5, samarium 6·9, erbium 7·4, aluminium 5·9. PAR has been used as an indicator for the spectrophotometric EDTA titration of erbium at pH 8·0–8·8, and, more recently, as a reagent for the spectrophotometric determination of lanthanum and cerium,[2] or of the sum of rare earths elements in neutral or slightly alkaline medium.[3,4]

It is generally assumed[3] that the composition of the complexes formed under these conditions is M:R = 1:2. This was not considered strange, because such complexes are sometimes formed with PAR in alkaline medium when there is a slight excess of PAR and when the formation is not hindered by hydrolysis. For lanthanum(III) and cerium(III) these complexes were also prepared in solid state.[2]

In this paper the complexation of aluminium, yttrium, lanthanum and lanthanides with PAR is studied in detail. No evidence for 1:2 complexes with the exception of that of yttrium can be found at pH $< 7{\cdot}5$. Thus the "normal" MR complex (H_2R = PAR) prevails under the conditions described earlier for the spectrophotometric determination of these elements. Results obtained by the method of continuous variations must be carefully evaluated for these systems.

EXPERIMENTAL

Only reagents and apparatus not described previously are listed.

Reagents

Metal-ion solutions. All chemicals used were analytically pure. Standard solutions of yttrium, lanthanide and lanthanum perchlorates, and aluminium and praseodymium nitrates were prepared

* See also: *Talanta*, 1966, **13**, 667; 1967, **14**, 171.

from the spectrally pure oxides (Johnson and Matthey). The solutions were standardized gravimetrically when the oxides dissolved were not well-defined.

Control of pH. The pH of solutions was regulated by addition of suitable amounts of 0·1, 0·5 and 2*M* ammonia or perchloric acid, and the ionic strength was adjusted to 0·1 by addition of sodium perchlorate.

Procedure for complexation studies

In the case of PAR the formation of MRH, MR, $M(RH)_2$ and MR_2 complexes and equilibria involving H_2R, HR^- and H_3R^+, where H_2R is electrically neutral PAR, is considered.

The pH-absorbance curves for equimolar solutions and solutions containing an excess of metal ion were interpreted by the help of the $C_R/A = f[H]^n$ transformations previously derived, or corresponding logarithmic plots.[5–7]

The true equilibrium is confirmed by the linearity of a suitable transformation and the number of protons split off. The molar absorptivities and stability constants of the complexes were found graphically.

Occasionally the method of continuous variations[8] was also used.

RESULTS AND DISCUSSION

Complexation of aluminium

Absorption curves for solutions at pH 3·66–4·9 when $C_M \geqslant C_R$ (Figs. 1 and 2) have isosbestic points. The measurements at pH >4·9 are complicated by hydrolysis. The limiting wavelength of maximum absorption and isosbestic point occur at 495 and 435 mμ respectively when $C_M = 3{\cdot}99 \times 10^{-3}M$ and $C_R = 3{\cdot}99 \times 10^{-5}M$ and at 490 and 430 mμ when $C_M = C_R = 5{\cdot}87 \times 10^{-5}M$ (C_M and C_R are the analytical concentrations of the metal and reagent, respectively).

Job's method indicates a 1:1 Al(PAR) complex (Fig. 3); curves at pH > 6 are unobtainable because of hydrolysis.

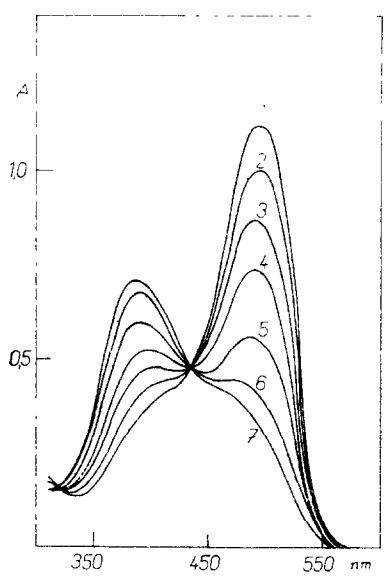

FIG. 1.—Absorption spectra for PAR-solutions with excess of aluminium. $C_R = 3{\cdot}99 \times 10^{-5}M$; $C_M = 3{\cdot}99 \times 10^{-3}M$. pH: *1*—4·39; *2*—4·28; *3*—4·19; *4*—4·10; *5*—3·98; *6*—3·79; *7*—3·66.

Absorbance-pH plots indicate rapid formation of a complex of limited stability over a narrow pH region at pH >3·5 for solutions with excess of aluminium ($C_M/C_R = 100$). In equimolar solutions with $C_M = C_R = 5{\cdot}87 \times 10^{-5}M$ this complex is only formed at pH >4·5 and the absorbance decreases with increase in pH because of hydrolysis at pH >5 (Fig. 4).

The splitting off of two protons during complexation was proved for solutions with an excess of aluminium by the linearity of the transformation (1) for $n = 2$ (Fig. 5):

$$C_R/A = \frac{1}{\varepsilon_1} + \frac{(A - \varepsilon_{R2}C_R)[H]^n}{\varepsilon_1 k_{1n} C_M} \tag{1}$$

(the ligand is present solely as H_2R in solution over the pH region studied).*

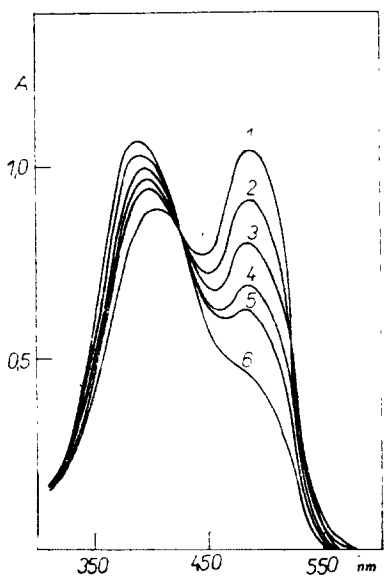

FIG. 2.—Absorption spectra for equimolar PAR and aluminium solutions. $C_R = C_M = 5{\cdot}871 \times 10^{-5}M$. pH: *1*—5·08; *2*—5·04; *3*—5·01; *4*—4·90; *5*—4·80; *6*—4·65.

This conclusion was confirmed by the corresponding log plot (2):

$$\log \frac{A - A_{0R}}{A_{01} - A} = n\text{pH} + \log C_M + \log k_{1n} \tag{2}$$

where $A_{01} = \varepsilon_1 C_R$ and $A_{0R} = \varepsilon_{R2} C_R$, *cf.* Fig. 6.

Because a 1:1 complex is evidently formed, one of the following equilibria must be valid:

$$Al^{3+} + H_2R \rightleftharpoons AlR^+ + 2H^+ \tag{A}$$

$$Al^{3+} + H_2R \rightleftharpoons Al(RH)(OH)^+ + 2H^+. \tag{B}$$

* Symbols have the same meaning as in earlier papers in this series. The definitions and values of the constants are summarized towards the end of this paper.

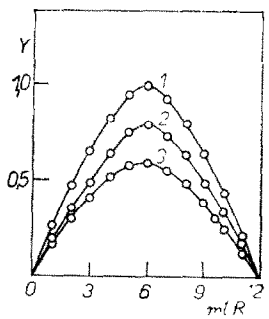

FIG. 3.—Job curves of equimolar PAR and aluminium solutions at 500 mμ. $C_{total} = 1{\cdot}068 \times 10^{-4}M$. pH: *1*—5·50; *2*—5·25; *3*—5·10.

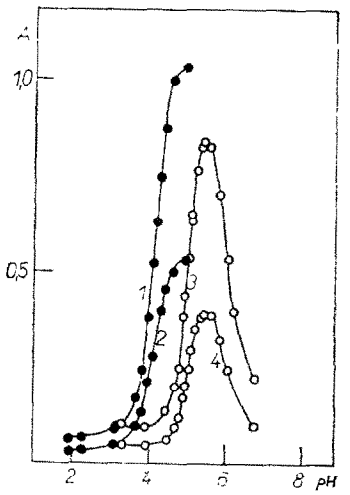

FIG. 4.—pH-Absorbance curves for PAR and aluminium solutions. $C_R = 3{\cdot}99 \times 10^{-5}M$; $C_M = 3{\cdot}989 \times 10^{-3}M$: *1*—520 mμ; *2*—530 mμ. $C_R = C_M = 5{\cdot}571 \times 10^{-5}M$: *3*—520 mμ; *4*—530 mμ.

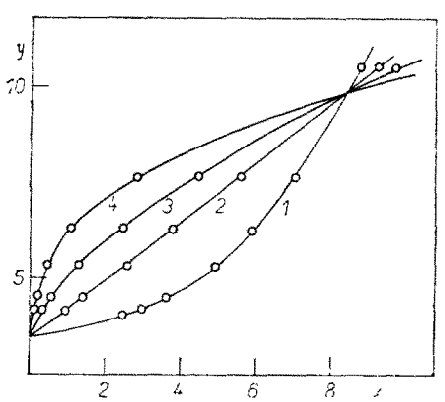

FIG. 5.—Analysis of Fig. 4, curve 1, according to equation (1). $y = C_R \times 10^5/A$; $x = (A - \varepsilon_{R2}C_R)\,[H]^n/A$: *1*—$n = 1$; $x \times 10^5$: *2*—$n = 2$; $x \times 10^9$: *3*—$n = 3$; $x \times 10^{13}$: *4*—$n = 4$; $x \times 10^{17}$.

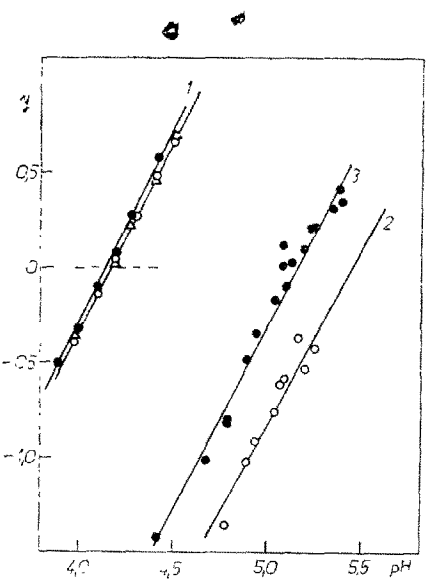

FIG. 6.—Log plots based on Fig. 4. *1*—according to equation (2); ● 500 mμ; ○ 520 mμ; △ 510 mμ. *2* and *3*—according to equation (4): 520 mμ and 530 mμ. $y = \log (A - A_{0R})/(A_{01} - A)$ or $(A - A_{0R})/(A_{01} - A)^2$.

Two protons are split off in equimolar solutions ($5 \times 10^{-5}M$) at pH < 5·4, where the H_2R form of the ligand predominates. This follows from the linearity of the transformation (3) and the logarithmic plot (4) (Fig. 6).

$$\frac{C_R}{A} = \frac{1}{\varepsilon_1} + \frac{[H]}{A\varepsilon_1}\sqrt{\frac{(\varepsilon_1 - \varepsilon_{R2})(A - \varepsilon_{R2}C_R)}{\kappa_{12}}} \tag{3}$$

$$\log \frac{A - \varepsilon_{R2}C_R}{(\varepsilon_1 C_R - A)^2} = 2\,\mathrm{pH} + \log \kappa_{12} - \log(\varepsilon_1 - \varepsilon_{R2})\,. \tag{4}$$

Thus equilibrium (A) is again established as the operative one. Moreover the values of molar absorptivity of the AlR^+ complex calculated from the intercepts of (1) and (3) are higher than is usual for an MRH-complex and closer to those expected for MR complexes (Table I).

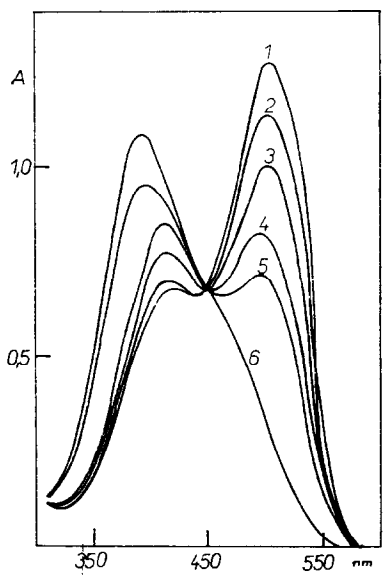

FIG. 7.—Absorption spectra for PAR-solutions with excess of yttrium. C_R = $5{\cdot}83 \times 10^{-5}M$; $C_M = 3{\cdot}54 \times 10^{-3}M$. pH: *1*—6·27; *2*—6·07; *3*—5·76; *4*—5·45; *5*—4·96; *6*—3·28.

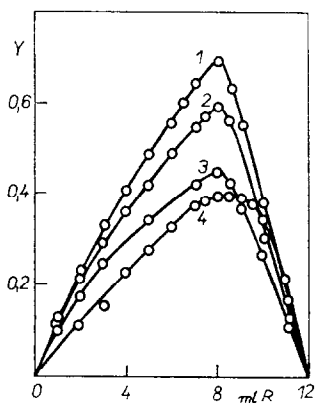

FIG. 8.—Job curves for equimolar PAR and yttrium solutions. $C_{total} = 7{\cdot}48 \times 10^{-5}M$; 500 mμ. pH: *1*—6·00; *2*—5·90; *3*—5·75; *4*—8·10 ($C_{total} = 8{\cdot}80 \times 10^{-6}M$; 0·008*M* triethanolamine).

Complexation of yttrium

Absorption curves have $\lambda_{max} = 500$ mμ at pH 6·07 and 490 mμ at pH < 6 and an isosbestic point at 450 mμ for solutions with an excess of metal ion between pH 3·28 and 6·27 (Fig. 7). The maximum of the curves for equimolar solutions is shifted to 510 mμ at pH 6·6.

Job curves suggest a $Y(PAR)_2$ complex between pH 5·5 and 8 (Fig. 8). At lower pH values the curves are deformed and the mole ratio M:R decreases. At pH > 6 the measurements are very difficult in equimolar solutions, owing to rapid fading of the colour.

A mutual transition of at least two complexes is shown from the pH-absorbance curves for solutions with excess of metal ion present (Fig. 9). One proton is evidently split off during complexation at pH < 5 according to the linearity of transformation (1) for $n = 1$, and the corresponding logarithmic plot (2) (Fig. 10, Fig. 11, curve 1).

Only equilibrium (C) need be considered in solutions containing excess of metal ion at pH 3·6–4·4:

$$Y^3 + H_2R \rightleftharpoons YRH^2 + H^+. \qquad (C)$$

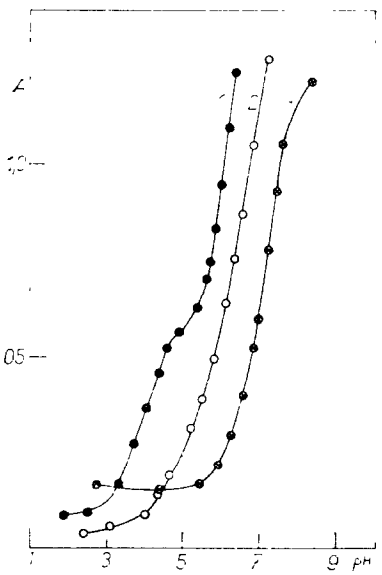

FIG. 9.—pH-absorbance plots for PAR and yttrium solutions. *1*—$C_R = 5{\cdot}83 \times 10^{-5}M$; $C_M = 3{\cdot}54 \times 10^{-3}M$; *2*—$C_R = C_M = 3{\cdot}97 \times 10^{-5}M$; *3*—$C_R = 5{\cdot}10 \times 10^{-5}M$; $C_M = 5{\cdot}10 \times 10^{-6}M$. $\lambda = 530$–520 mμ.

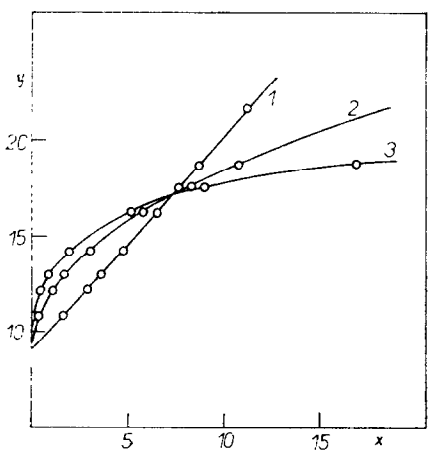

FIG. 10.—Graphical analysis of Fig. 9, curve 1, according to equation (1). $y = C_R \times 10^5/A$, $x = (A - \varepsilon_{R_2}C_R)[H]^n/A$. *1*—$n = 1$; $x \times 10^5$: *2*—$n = 2$; $x \times 10^9$: *3*—$n = 3$; $x \times 10^{13}$.

The splitting off of one proton between pH 5·8 and 6·4 was assumed to be due to a mutual transition of two complexes, according to (D), rather than to the formation of $Y(RH)_2^+$.

$$YRH^{2+} \rightleftharpoons YR^+ + H^+. \qquad (D)$$

The linearity of transformation (5) agrees well with this assumption, and the precise value of $n = 1$ follows from the logarithmic plot (6) (Fig. 11).

$$\frac{C_R}{A} = \frac{1}{\varepsilon_1} + \frac{(A - \varepsilon_{1H}C_R)[H]}{A}\,\frac{1}{K_{kal}\varepsilon_1} \qquad (5)$$

$$\log\frac{A - \varepsilon_{1H}C_R}{\varepsilon_1 C_R - A} = pH + \log K_{kal}. \qquad (6)$$

For $\lambda < 520$ mμ and at pH < 5·6 or >7 other equilibria were indicated by the larger scattering of points for the plot of equation (5).

For equimolar solutions (*cf.* Fig. 9) linearity is only obtained with transformation

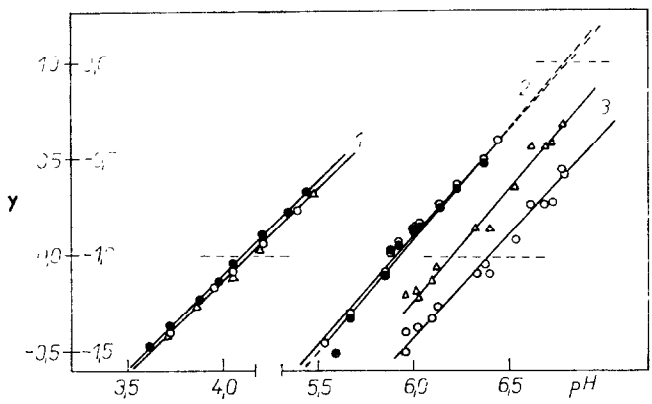

FIG. 11.—Logarithmic analysis of the pH-absorbance plots.
1—according to equation (2): ○ 520 mμ; △ 510 mμ; ● 530 mμ. *2*—according to equation (6): ○ 520 mμ ; ● 530 mμ (right-hand *y*-scale). *3*—according to equation (8): 520 mμ; *4*—530mμ. $y = \log (A - A_{0R})/(A_{01} - A)$, $\log (A - A_{01})/(A_{02} - A)$, and $\log (A - A_{0R})/(A_{01} - A)^2$ respectively.

(7), derived for 1:1 complex formation with loss of one proton, and in logarithmic transformation (8) from which $n = 1$ was found for 520–530 mμ.

$$\frac{C_R}{A} = \frac{1}{\varepsilon_1} + \frac{\sqrt{[H](A - \varepsilon_{R3}C_R)}}{A}\frac{1}{\varepsilon_1}\sqrt{\frac{\varepsilon_1 - \varepsilon_{R3}}{\kappa_{11}}} \tag{7}$$

$$\log\frac{A - \varepsilon_{RX}C_R}{(\varepsilon_1 C_R - A)^2} = n\text{pH} + \log\kappa_{1n} - \log(\varepsilon_1 - \varepsilon_{RX}). \tag{8}$$

Hence the equilibrium (E) obtains for equimolar solutions at pH 5·9–7·2:

$$Y^{3+} + HR^- \rightleftharpoons YR^+ + H^+. \tag{E}$$

Complexation of lanthanum

The formation of complexes in solutions where $C_M \geqslant C_R$ is greatly disturbed by the hydrolysis of lanthanum.

The absorption curves have λ_{max} 510 mμ at pH > 7 and an isosbestic point at 455 mμ between pH 6·22 and 7·35 for solutions with $C_M/C_R = 10$, (Fig. 12).

The graphical analysis of the pH-absorbance plots for solutions with slight excess of metal ion coincides with the formation of a 1:1 complex only between pH 6 and 7. The HR^- anion is practically the only form of ligand in solution under these conditions. The transformation (9) is linear, showing the splitting off of one proton:

$$\frac{C_R}{A} = \frac{1}{\varepsilon_1} + \frac{(A - \varepsilon_3 C_R)[H]}{A\kappa_{11}\varepsilon_1} \tag{9}$$

(Figs. 13, 14).

A straight line with slope $n = 0{\cdot}9$ was found for the logarithmic transformation (2) at 510–530 mμ and pH 6·0–6·5 (Fig. 15).

Higher values for n were found at pH > 6·6 and the formation of a further complex cannot be excluded. The use of Job's method is hindered by hydrolysis. Only the equilibrium (F) can be proved with certainty in this case:

$$La^{3+} + HR^- \rightleftharpoons LaR^+ + H^+. \tag{F}$$

Complexation of lanthanides

Absorption curves have a limiting maximum at 500 mμ and an isosbestic point at 445 mμ for pH 6·3–6·5 and for $C_M/C_R = 100$ for praseodymium, neodymium, samarium, dysprosium, erbium and ytterbium (Fig. 16).

The pH-absorbance plots indicate the presence of at least two red complexes in solutions containing excess of metal ion (Fig. 17), one at pH < 4, the other between pH 4 and 6.

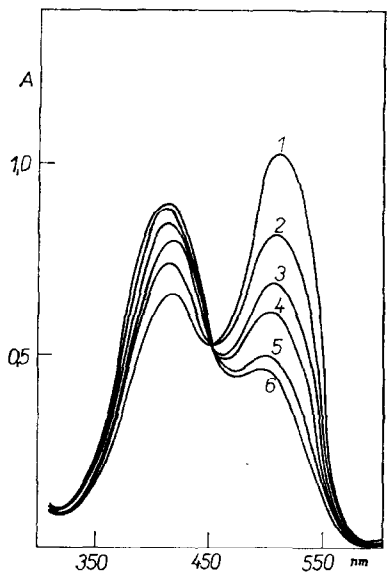

FIG. 12.—Absorbance curves for PAR-solutions with excess of lanthanum. $C_R = 4{\cdot}30 \times 10^{-5}M$, $C_M = 7{\cdot}30 \times 10^{-4}M$ pH: *1*—7·35; *2*—7·06; *3*—6·80; *4*—6·70; *5*—6·29; *6*—6·22.

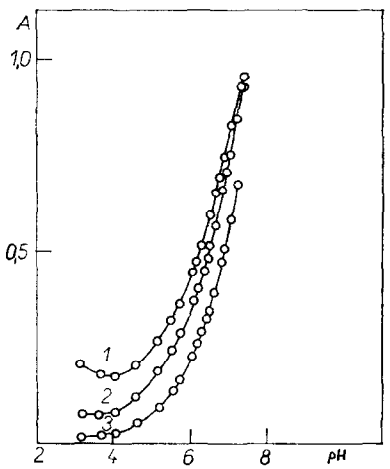

FIG. 13.—pH-Absorbance plot for PAR solutions with excess of lanthanum. $C_R = 4{\cdot}30 \times 10^{-5}M$, $C_M = 4{\cdot}30 \times 10^{-4}M$. *1*—500 m$\mu$; *2*—520 m$\mu$; *3*—540 m$\mu$.

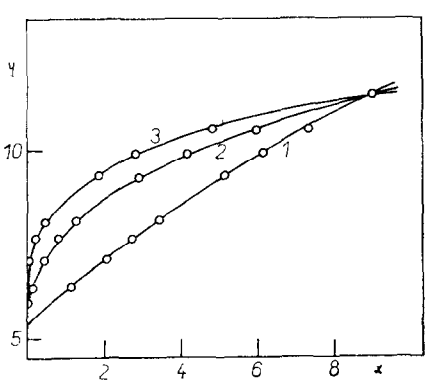

FIG. 14.—Graphical analysis of pH-absorbance plot (at 510 mμ, same conditions as Fig. 13) according to equation (9). $y = C_R 1 \times 0^5 A$, $x = (A - \varepsilon_{R3})[H]^n/A$. *1*—$n = 1$; $\times x 10^7$: *2*—$n = 2$; $x \times 10^{13}$: *3*—$n = 3$; $x \times 10^{19}$.

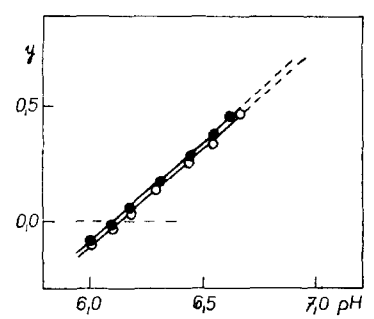

FIG. 15.—Logarathmic plots according to equation (2), for same conditions as for Fig. 13. ○ 510 mμ, ● 520 mμ $A_{0R} = \varepsilon_{R3}C_R$, $A_{01} = \varepsilon_1 C_R$.

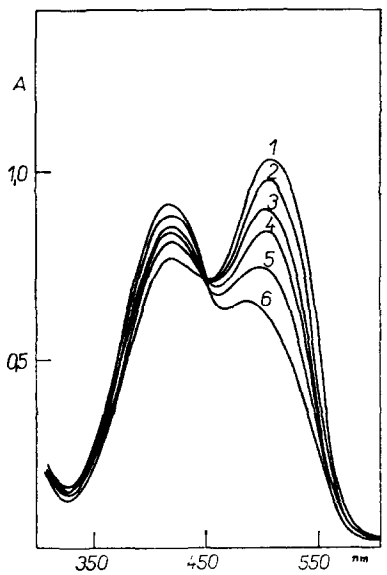

FIG. 16.—Absorption curves for PAR solutions with excess of praseodymium. $C_R = 5{\cdot}59 \times 10^{-5}M$, $C_M = 5{\cdot}59 \times 10^{-3}M$. pH: *1*—6·48; *2*—6·36; *3*—6·23; *4*—6·10; *5*—5·82; *6*—4·97.

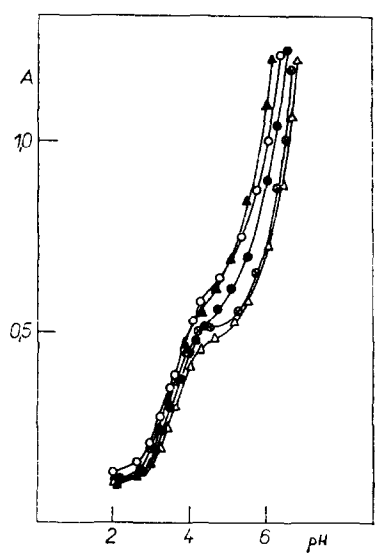

FIG 17.—pH-Absorbance plots (520 mμ) for PAR solutions with lanthanide ions in excess.

○ Er^{3+}: $C_R = 5{\cdot}01 \times 10^{-5}M$, $C_M = 2{\cdot}64 \times 10^{-3}M$
▲ Yb^{3+}: $C_R = 5{\cdot}27 \times 10^{-5}M$, $C_M = 1{\cdot}51 \times 10^{-3}M$
⊕ Sm^{3+}: $C_R = 5{\cdot}27 \times 10^{-5}M$, $C_M = 1{\cdot}92 \times 10^{-3}M$
● Dy^{3+}: $C_R = 5{\cdot}27 \times 10^{-5}M$, $C_M = 1{\cdot}98 \times 10^{-5}M$
△ Nd^{3+}: $C_R = 5{\cdot}27 \times 10^{-5}M$, $C_M = 1{\cdot}84 \times 10^{-3}M$

It was assumed that all the lanthanides would react with PAR similarly, but that slight differences in the stabilities of individual complexes would influence the position and shape of pH-absorbance plots.

One proton is split off during complexation between pH 3·15 and 4·2. The transformation (10), derived on the assumption of the partial existence of the protonated ligand, H_3R^+, over the pH range studied, has a linearity only for $n = 1$ as proved for praseodymium and samarium (Fig. 18):

$$\frac{C_R}{A} = \frac{1}{\varepsilon_{1H}} + \frac{A(1 + [H]/K_{a1}) - A_{0R}}{AC_M\varepsilon_{1H}k_{11}}[H] \qquad (10)$$

where

$$A_{0R} = \varepsilon_{R1}C_R\frac{[H]}{K_{a1}} - \varepsilon_{R2}C_R.$$

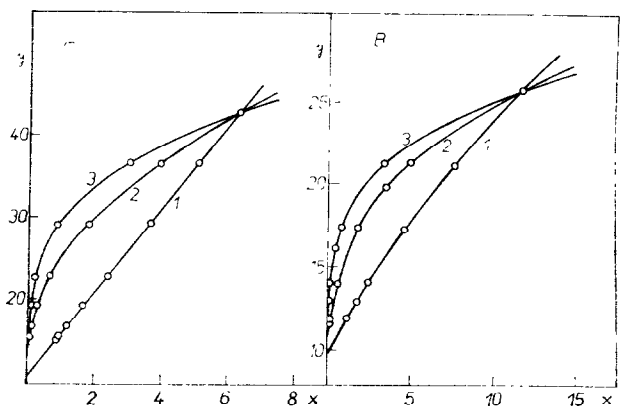

FIG. 18.—Graphical analysis of the first part of pH absorbance plots (at 520 mμ) for praseodymium and samarium solutions in excess (*cf.* Fig. 17) according to equation (10). $y = C_R \times 10^5/A$; $x = \{A(1 + [H]/K_{a1}) - A_{0R}\}[H]^n/A$. A: Pr^{3+}; B: Sm^{3+}. *1*—$n = 1$; $x \times 10^4$: *2*—$n = 2$; $x \times 10^7$: *3*—$n = 3$; $x \times 10^{10}$.

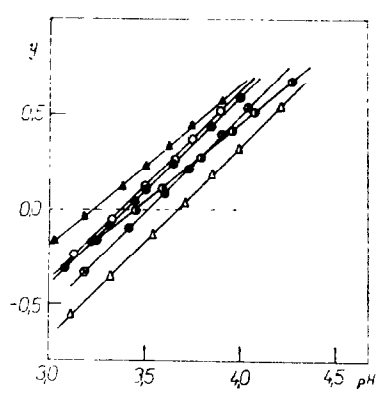

FIG. 19.—Logarithmic analysis of the pH-absorbance plots for lanthanide solutions (*cf.* Fig. 17, first part) according to equation (11).
▲ Sm^{3+}; ○ Dy^{3+}; ● Yb^{3+}; ◑ Er^{3+}; ⊕ Nd^{3+}; △ Pr^{3+}.

Slopes approaching unity ($n = 0{\cdot}8-1{\cdot}0$) were found when the logarithmic function (1) was plotted for solutions containing excess of various lanthanide ions (Fig. 19):

$$\log \frac{A(1 + [H]/K_{a1})}{A_{01} - A} = pH + \log C_M + \log k_{11} \qquad (11)$$

where $A_{01} = \varepsilon_{1H} C_R$.

Absorbances at 510–530 mμ and molar absorptivities calculated from equation (10) were used. Deviations in the erbium system are probably caused by a further complex formed under the same conditions, pH > 4.

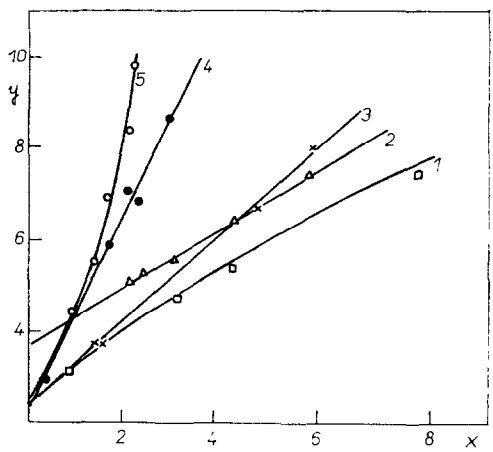

FIG. 20.—Graphical analysis of the second part of pH-absorbance plots (at 530 mμ; *cf.* Fig. 17) according to equation (5).
1—Yb^{3+}; *2*—Er^{3+}; *3*—Dy^{3+}; *4*—Sm^{3+}; *5*—Nd^{3+}; $y = C_R \times 10^5/A$, $x = (A - A_{01})[H] \times 10^7/A$.

Analysis of the pH-absorbance curves by equations (5) and (6) for reactions over the pH range 5·4–7·2, the wavelength of absorption being $\geqslant$ 530 mμ, showed that one proton was split off during complexation (Figs. 20, 21). Thus for solutions of PAR containing a slight excess of lanthanide ion, equilibrium (6) was proved when pH < 4 and (H) when pH > 5·4:

$$M^{3+} + H_2R \rightleftharpoons MRH^{2+} + H^+ \qquad (G)$$

$$MRH^{2+} \rightleftharpoons MR^+ + H^+. \qquad (H)$$

In equimolar solutions ($7{\cdot}45 \times 10^{-5} M$) equilibrium (I) is valid as indicated by the pH-absorbance plot for praseodymium (Fig. 22).

$$M^{3+} + HR^{--} \rightleftharpoons MR^+ + H^+ \qquad (I)$$

The transformation (7) and the logarithmic plot (8) are linear giving a value of $n = 1{\cdot}1$ between pH 6·5 and 7·4 (Fig. 23).

The complex formed at pH 6·5–7·0 was shown by Job's method at 520 mμ and $C_{total} = 1{\cdot}490 \times 10^{-4} M$, to have a mole ratio of 1:1 (Fig. 24). In the praseodymium system the maximum of the Job curves at 520 mμ is shifted to a higher mole fraction of PAR, *i.e.*, 0·56–0·71 at pH 8, ($C_{total} = 1{\cdot}486 \times 10^{-4} M$) in the presence of 0·01 M

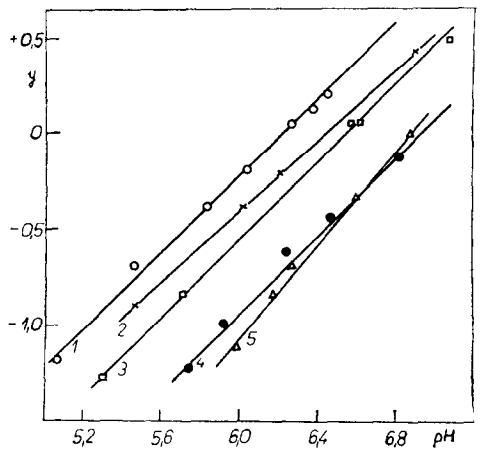

FIG. 21.—Logarithmic analysis of the second part of pH-absorbance plots (at 530 mμ; *cf.* Fig. 17) according to equation (11).
$y = \log (A - A_{01})/(A_{02} - A)$. *1*—$Dy^{3+}$; *2*—$Yb^{3+}$; *3*—$Er^{3+}$; *4*—$Sm^{3+}$; *5*—$Nd^{3+}$.

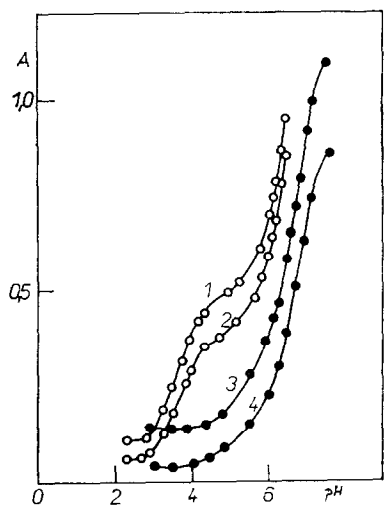

FIG. 22.—pH-Absorbance plot for PAR solutions with praseodymium.
$C_R = 5{\cdot}59 \times 10^{-5}M$, $C_R = 5{\cdot}59 \times 10^{-3}M$: *1*—520 mμ; *2*—530 mμ.
$C_M = C_R = 7{\cdot}45 \times 10^{-5}M$; *3*—520 mμ; *4*—540 mμ.

triethanolamine. The absorbance decreases rapidly with time, the part of the curves where metal ion is in excess is deformed and the maximum is also continuously shifted. This suggests the influence of hydrolysis rather than a 1:2 complex as suggested earlier.

As no evidence was found for a 1:2 lanthanide-PAR complex in solutions the assumption of Munshi and Dey[3] could not be substantiated.

Optical and equilibrium constants

The molar absorptivities calculated in various ways are collected in Tables I and II. The values of molar absorptivities for the MR complex sometimes lack high

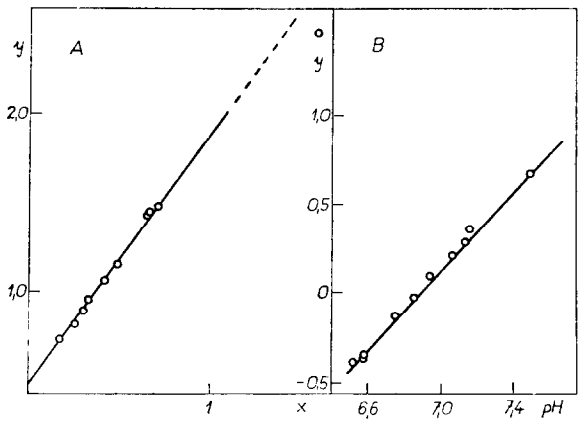

FIG. 23.—Graphical analysis of the equimolar pH-absorbance plot for praseodymium and PAR solutions (*cf.* Fig. 22).
A. According to equation (7), $y = C_R \times 10^5/A$,
$x = \sqrt{[H](A - \varepsilon_{R_3}C_R)} \times 10^3/A$.
B. According to equation (8), $y = \log (A - A_{0R})/(A_{01} - A)^2$.

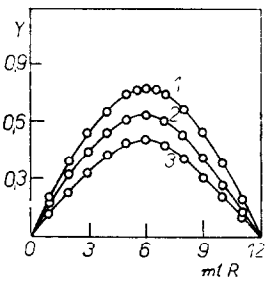

FIG. 24.—Job curves for equimolar PAR and praseodymium solutions, at 520 mμ.
$C_{total} = 1{\cdot}49 \times 10^{-4}M$.
pH: *1*—7·00; *2*—6·75; *3*—6·50.

TABLE I.—MOLAR ABSORPTIVITIES OF PARTICULAR COMPLEXES

Element	Molar absorptivities, $\varepsilon \times 10^{-4}$ MRH			MR		
	510 mμ	520 mμ	530 mμ	510 mμ	520 mμ	530 mμ
Al	—	—	—	3·64*	2·90*	1·44*
					3·6†	1·3†
Y	1·44*	1·10*	1·48*		4·7‡‡	4·3‡‡
					3·9††	3·3††
La	—	—	—	1·85‡	1·70‡	1·48‡
Pr	1·09**	0·90**	0·73**			2·0††
Nd	1·06**	0·97**	0·79**			4·0‡‡
Sm	1·15**	1·04**	0·86**			4·1‡‡
Dy	1·12**	0·97**	0·79**			2·7‡‡
Er	1·59**	1·37**	1·10**			4·1‡‡
Yb	1·30**	1·18**	1·01**			4·0‡‡

* from equation (1), † from equation (3), ‡ from equation (9),
** from equation (10), †† from equation (7), ‡‡ from equation (5).

TABLE II.—CONSTANTS FOR PAR-COMPLEXES WITH SOME GROUP III ELEMENTS

Element	$\log k_{11}$	$\log \kappa$	$\log K_{1H}$	$\log K_{kbl}$	$\log K_1$
Al	—	−5·9*; $-6{\cdot}2_5$*	—	—	11·6; 11·3
Y	−1·67	$-1{\cdot}7_5$†	10·2	−6·7	9·1
La	—	$-2{\cdot}7_4$†	—	—	9·2
Pr	−1·41	−2·6†	10·5	—	9·3
Nd	−0·78	—	11·1	−6·9	9·8
Sm	−0·52	—	11·4	−6·9	10·1
Dy	−0·68	—	11·2	−6·2	10·6
Er	−0·87	—	11·0	−6·5	10·1
Yb	−0·83	—	11·1	−6·5	10·2

* κ_{12}, † κ_{11}.

precision. For lanthanides the values for 510–520 mμ were not calculated because of the high errors involved. The following equilibrium and stability constants were evaluated:

$$k_{11} = [MRH][H]/[M][H_2R] \qquad K_{1H} = [MRH]/[M][RH^*]$$
$$\kappa_{12} = [MR][H]^2/[M][H_2R] \qquad K_1 = [MR]/[M][R]$$
$$\kappa_{11} = [MR][H]/[M][HR^*] \qquad K_{kal} = [MR][H]/[MRH]$$

where HR* is the hypothethetical anion derived if the *o*-hydroxy group dissociates first. Some further relations between particular constants are valid:

$$K_{1H} = k_{11}/K_{a2}^*$$
$$K_1 = K_{kal} \cdot K_{1H}/K_{a3}^*$$
$$K_1 = \kappa_{12}/K_{a2}K_{a3} = \kappa_{11}/K_{a3}^*$$

where $K_{a2}^* = K_{a3}$ and $K_{a3}^* = K_{a2}$ (see *Talanta*, 1967, **14**, 182).

The equilibrium constants were calculated from the intercepts of the logarithmic plots (2, 4, 6, 8, 11). The data are summarized in Table II.

With the exception of aluminium, the Group III B elements form more stable PAR complexes than the Group III A elements do.[9–12] The same is true for the complex binding tendency of these metals ($\log k_{11}$, $\log k_{12}$, $\log \kappa_{12}$, $\log \kappa_{11}$).

Little difference in stability was found between corresponding protonated and "normal" complexes but a considerable increase in absorptivity for the latter complexes was observed. The "normal" species seem to be slightly less stable. There is no simple relation between complex stability and atomic number or radius of the lanthanides; however, as expected, the stabilities do not differ considerably.

The "normal" MR complex is only suitable for the spectrophotometric determination of yttrium and lanthanides in slightly acid, neutral and alkaline medium. Care must be taken to ensure that only this complex is formed in solution because variable proportions of the protonated and "normal" complexes greatly affect the results. Moreover the 1:2 complex formed in solutions containing excess of ligand also influences the apparent molar absorptivity and the sensitivity of the method.

Hence the working conditions (pH, excess of ligand, metal ion concentration region, the ionic strength and the buffering substances) must be carefully maintained for the standard and sample solutions, otherwise confusing results are obtained.

PAR has no advantage as a colorimetric reagent for aluminium and lanthanum.

Acknowledgement—We are indebted to Dr. M. Hniličková for helpful discussions.

Zusammenfassung—Die empfindlichen Reaktionen zwischen 4-(2-Pyridylazo)resorcin (PAR) und Yttrium, Lanthan und den Lanthaniden können zur spektrophotometrischen Bestimmung dieser Elemente benutzt werden. Die Methode hat keine Vorteile gegenüber anderen Methoden zur Bestimmung von Aluminium und Lanthan. Nur M(PAR)H- und M(PAR)-Komplexe werden in Lösungen gebildet, in denen die Molarität des Ions größer oder gleich der Molarität des Liganden bei pH < 7,5 ist. Wenn molarer Überschuß an PAR besteht, konnen 1:2-Komplexe gebildet werden, aber sicher ist das nur für das Yttrium-PAR-System. Fehler in der Analyse können vom gleichzeitigen Vorhandensein optisch verschiedener Komplexe herrühren. Eingehende Kontrolle von pH und Konzentration des Reagens ist wichtig. Es werden optische und Gleichgewichtsdaten für die untersuchten Systeme angegeben.

Résumé—On peut utiliser les réactions sensibles entre le 4-(2-pyridylazo) résorcinol (PAR) et l'yttrium, le lanthane et les lanthanides pour le dosage spectrophotométrique de ces éléments. La méthode n'offre pas d'avantages par rapport aux autres pour les dosages de l'aluminium et du lanthane. Seuls les complexes M (PAR) H et M (PAR) se forment dans des solutions où la molarité de l'ion metallique est supérieure ou égale à la molarité du ligand à pH $< 7{,}5$. S'il y a un excès molaire de PAR, des complexes 1:2 peuvent se former, mais ceci n'est certain que pour le système yttrium-PAR. Des erreurs d'analyse peuvent résulter de la présence simultanée de complexes optiquement différents; un contrôle serré du pH et de la concentration en réactif est essentiel. On fournit des données optiques et sur l'équilibre pour les systèmes étudiés.

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SPECTROPHOTOMETRIC DETERMINATION OF SCANDIUM WITH BROMOPYROGALLOL RED

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Summary—A highly sensitive spectrophotometric method for scandium with Bromopyrogallol Red is described; microgram amounts of scandium can be determined by measurement at 610 mμ and pH 6·1. The molar absorptivity is $2{\cdot}4 \times 10^4$ at 610 mμ. Formation of a 1:1 complex of scandium with Bromopyrogallol Red is confirmed. Common cations interfere, but can be separated completely by three successive ion-exchange steps, so the method can be applied to the determination of traces of scandium in silicate rocks. Results are quoted for scandium in several types of igneous rocks.

FOR the spectrophotometric determination of scandium, Sandell[1] in 1959 considered two reagents, Alizarin Red S and 8-quinolinol, and also described a method using Morin. Recently, many other organic reagents have been used for the spectrophotometric determination of scandium. All these reagents are more sensitive than Alizarin Red S and 8-quinolinol but are not selective.

Jeníčková, Suk and Malát[2] proposed Bromopyrogallol Red, (5,5′-dibromopyrogallol sulphophthalein), as a metal indicator for complexometric titration of the rare earth elements. The reagent has since been applied to the spectrophotometric determination of a number of elements such as indium,[3] niobium,[4] silver[5] and uranium.[6]

The present author has found that Bromopyrogallol Red is a very sensitive colorimetric reagent for scandium. For comparison, the molar absorptivities of various scandium complexes are listed in Table I. Bromopyrogallol Red is not, however, as selective as other colorimetric reagents for scandium, and a preliminary separation must be made. This can be done by ion-exchange. The method is useful for determining traces of scandium in silicate rocks.

EXPERIMENTAL

Apparatus

A Shimazu Model QR-50 spectrophotometer with 1-cm cells was used for all absorbance measurements, and a Toa-denpa Model HM-5A pH meter with glass and calomel electrodes for pH measurement.

Reagents

Bromopyrogallol Red solution. 0·05% in 50% v/v aqueous ethanol.

Scandium stock solution. An appropriate amount of scandium oxide (99·9% purity) was dissolved in a minimum amount of diluted sulphuric acid, and the solution was evaporated to dryness. The residue was taken up in 100 ml of 0·05*M* sulphuric acid. The strength of the solution was determined by titration with 0·01*M* EDTA solution previously standardized against zinc metal of primary standard quality. The stock solution contained 0·860 mg of scandium per ml and was used after appropriate dilution.

Acetate buffer solution. 10 ml of 1*M* acetic acid were mixed with 320 ml of 1*M* sodium acetate to give a pH of 6·1.

Cation-exchange column (I). Five g of Dowex 50W-X8, 100–200 mesh (hydrogen form) were slurried with water to form a column 10 cm long and 1 cm in diameter.

Anion-exchange column (II). Ten g of Dowex 1-X8, 100–200 mesh, (sulphate form) were formed into a column 18 × 1 cm. Before use the column was washed with several column volumes of 0·1 *M* ammonium sulphate–0·025*M* sulphuric acid solution.

Anion-exchange column (III). Two g of Dowex 1-X8, 100–200 mesh, (chloride form) were formed into a column 3 × 1 cm. The column was pretreated with 6*M* hydrochloric acid before use.

All other reagents used were guaranteed reagent grade.

Procedure

Transfer to a 25 ml volumetric flask 10 ml of dilute sulphuric acid solution containing between 3 and 70 μg of scandium. Add 3 ml of the Bromopyrogallol Red solution and 5 ml of acetate buffer solution. Dilute to the mark with water, mix, and measure the absorbance of the solution at 610 mμ against a reagent blank. The final pH should be 6·1.

Construct a calibration curve covering the range 5–70 μg of scandium.

TABLE I.—COMPARISON OF SENSITIVITY OF COLORIMETRIC REAGENTS FOR SCANDIUM

Reagents	Molar absorptivity	Reference
Alizarin Red S	$4·8 \times 10^3$ (at 520 mμ)	1
8-Quinolinol	$7·5 \times 10^3$ (at 378 mμ)	1
Tiron	$8·1 \times 10^3$ (at 310 mμ)	7
5,7-Dichloro-8-quinolinol	$1·0 \times 10^4$ (at 397 mμ)	8
Anthrarufin-2,6-disulphonic acid	$1·1 \times 10^4$ (at 495 mμ)	9
Chlorophosphonazo-III	$1·2 \times 10^4$ (at 690 mμ)	10
Quercetin	$1·3 \times 10^4$ (at 435 mμ)	11
4-(2-Pyridylazo)-resorcinol	$1·5 \times 10^4$ (at 520 mμ)	12
Arsenazo	$1·7 \times 10^4$ (at 570 mμ)	13
Eriochrome Cyanine R	$1·9 \times 10^4$ (at 535 mμ)	14
Xylenol Orange	$2·4 \times 10^4$ (at 553 mμ)	15
Bromopyrogallol Red	$2·4 \times 10^4$ (at 610 mμ)	
Pontachrome Azure Blue B	$3·4 \times 10^4$ (at 610 mμ)	16

COLOUR REACTIONS OF SCANDIUM AND OTHER IONS

Absorption spectrum

The absorption spectrum of the solution was measured against a reagent blank at pH 6·1, and is shown in Fig. 1.

Effect of acidity

Acidity has a considerable effect on the absorbance of the complex at 610 mμ, as illustrated in Fig. 2. The maximum absorbance of the complex remains nearly constant in the pH range 5·0–6·5. Buffers of acetic acid–sodium acetate, hydrochloric acid–potassium chloride, and ammonia–ammonium chloride, were used to cover the pH ranges 2·7–6·1, 1·0–2·4, and 6·9–9·2 respectively.

Effect of reagent concentration

In order to study the effect of reagent concentration on the absorbance, 38·2 μg of scandium were added to solutions containing varying amounts of Bromopyrogallol Red solution and diluted to 25 ml, the total acetate concentration being kept constant. The reagent concentration had no effect on the absorbance when more than 2 ml of 0·05% Bromopyrogallol Red solution were present. The use of 3 ml of the reagent solution is recommended.

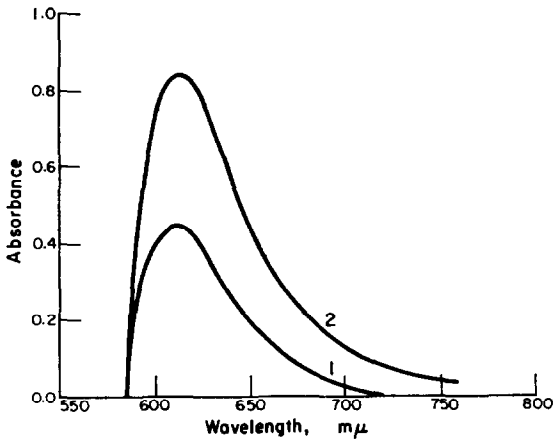

FIG. 1.—Absorption spectra for scandium–Bromopyrogallol Red complex at pH 6·1.
(1) Reagent ($1{\cdot}59 \times 10^{-6}$ mole) plus Sc (19·1 μg) per 25 ml, *vs.* reagent blank.
(2) Reagent ($1{\cdot}59 \times 10^{-6}$ mole) plus Sc (38·2 μg) per 25 ml, *vs.* reagent blank.

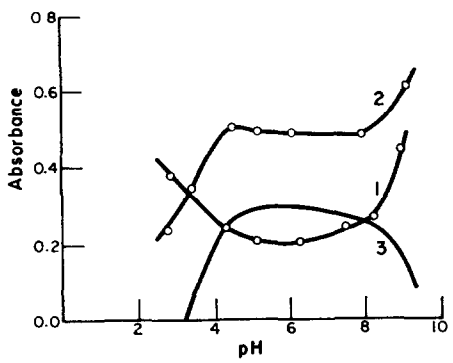

FIG. 2.—Effect of acidity on scandium–Bromopyrogallol Red complex at 610 mμ.
(1) Reagent blank ($1{\cdot}05 \times 10^{-6}$ mole/25 ml) *vs.* water.
(2) Reagent ($1{\cdot}05 \times 10^{-6}$ mole) plus Sc (14·3 μg) per 25 ml, *vs.* water.
(3) Reagent ($1{\cdot}05 \times 10^{-6}$ mole) plus Sc (14·3 μg) per 25 ml, *vs.* reagent blank.

Effect of buffer solution

At pH 6·1, the absorbance of the complex decreased very slightly as the concentration of acetate buffer increased. With increasing volumes of 4, 6, 8, and 10 ml of acetate buffer solution, the absorbance due to 19·1 μg of scandium decreased slightly, having the values 0·399, 0·395, 0·384, and 0·380 respectively. An addition of 5 ml of acetate buffer solution was chosen.

Stability of the coloured solution

The scandium–Bromopyrogallol Red complex formed almost instantly at pH 6·1 and the absorbance remained constant for at least 24 hr.

Conformity to Beer's law

The relationship between the absorbance of the scandium–Bromopyrogallol Red complex and the scandium concentration was examined by varying the scandium

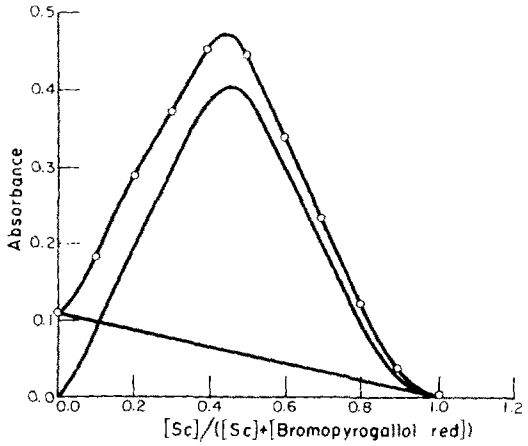

FIG. 3.—Continuous variation plots for scandium–Bromopyrogallol Red complex at pH 6·1 and 610 mμ.

TABLE II.—EFFECT OF DIVERSE IONS ON DETERMINATION OF 28·7 μg OF SCANDIUM

Ion	Amount added, *mg*	Sc found, *μg*
Al(III)	0·1	18·5
Be(II)	0·1	14·5
Cd(II)	0·1	21·0
Cr(III)	0·1	39·6
Cu(II)	0·1	∞
Er(III)	0·1	55·7
Fe(II)	0·1	62·2
Fe(III)	0·1	57·8
Ga(III)	0·1	64·3
In(III)	0·1	38·2
La(III)	0·1	42·2
Mn(II)	0·1	25·0
Mo(VI)	0·1	36·1
Ni(II)	0·1	34·5
Sm(III)	0·1	37·8
Sn(IV)	0·1	32·5
Th(IV)	0·1	48·5
Ti(IV)	0·1	∞
U(VI)	0·1	40·0
V(IV)	0·1	62·8
Y(III)	0·1	74·2
Zn(II)	0·1	38·1
Zr(IV)	0·1	35·0
Phosphate	20	2·0
Tartrate	20	11·7
Thiocyanate	20	15·2
Chloride	15·6	26·8
Chloride	31·2	22·8
Chloride	62·5	21·7
Chloride	93·7	19·3

concentration and measuring the absorbance at 610 mμ and pH 6·1. Conformity to Beer's law was found in the range 0·12–2·40 ppm of scandium. The molar absorptivity for scandium at 610 mμ was $2{\cdot}4 \times 10^4$.

Composition of the scandium–Bromopyrogallol Red complex

To estimate the empirical formula of the complex species formed under the present conditions, Job's method[17] of continuous variation and the slope-ratio method[18] were used, at pH 6·1 and 610 mμ. Figure 3 shows that the combining ratio of bromopyrogallol red to the scandium can be regarded as 1:1, and this was confirmed by the slope-ratio method.

Effect of diverse ions

The interference of many ions in the determination of scandium was studied under the conditions used in the procedure above. The results are summarized in Table II. Many common cations seriously interfere, but 0·1 mg of arsenic(III), bismuth(III),

TABLE III.—DETERMINATION OF SCANDIUM IN ROCK SAMPLES

Samples	Scandium content, *ppm*	
	Bromopyrogallol Red method	Arsenazo method[21]
Basalt	35·1, 36·8, 37·1 (mean 36·3 ± 1·1)	34·7 ± 1·2 (mean of 8)
Andesite	16·0, 16·1, 17·5, 18·6 (mean 17·1 ± 1·5)	20·7 ± 1·3 (mean of 12)
Quartz diolite	10·5, 11·6, 12·7 (mean 11·6 ± 1·1)	11·9 ± 1·2 (mean of 8)
Basalt composite	19·1, 21·6, 23·9 (mean 21·5 ± 2·4)	
Gabbro composite	18·8, 19·9 (mean 19·3)	
Diabase composite	17·7	
Andesite composite	14·3	
Composite of granite and granodiolite	6·2, 6·4, 6·6 (mean 6·4 ± 0·2)	

calcium, cobalt(II), magnesium and tungsten(VI) do not interfere. Sulphate, borate, nitrate and perchlorate do not interfere, but phosphate, thiocyanate, tartrate and large amounts of chloride must be absent. Because of the many interferences involved, a preliminary separation is necessary. In the following section a general procedure, including the preliminary separation by three ion-exchange steps, is given for the determination of scandium in silicate rocks. Although there have been reported several excellent ion-exchange systems for scandium, none of these appears to give complete enough separation for the subsequent photometric determination of scandium. A combination of the three ion-exchange steps allows the subsequent determination of scandium in complex matrix materials.

DETERMINATION OF SCANDIUM IN SILICATE ROCKS

Decompose a rock sample, weighing about 0·5 g, with a perchloric acid–hydrofluoric acid mixture and evaporate the solution to dryness. Dissolve the residue with dilute hydrochloric acid. Add a slight excess of 1:1 ammonia solution to the hot solution, filter off the precipitate and dissolve it with 20 ml of 3*M* hydrochloric acid. Load the solution on to the cation-exchange column (I) and wash the column with 10 ml of water, and then with 20 ml of 0·3*M* ammonium sulphate–0·025*M* sulphuric acid solution. Strip the scandium with 15 ml of the same eluent at a flow-rate of 0·7 ml/min. Add 30 ml of 0·025*M* sulphuric acid to the effluent. Load the solution on to the anion-exchange column (II). Remove foreign ions by elution with 45 ml of 0·1*M* ammonium sulphate–0·025*M* sulphuric acid solution and elute the scandium with a further 130 ml of the same solution. Add 10 mg of iron(III) to the effluent and precipitate iron(III) hydroxide with ammonia solution. Filter off the precipitate and dissolve it in 10 ml of 6*M* hydrochloric acid. Pass the solution through the anion-exchange

column (III). Wash the column with 6*M* hydrochloric acid. Collect all the hydrochloric acid solution and evaporate it to dryness. Dissolve the residue in 1 ml of 0·1*M* sulphuric acid and dilute to 10 ml with water. Continue as described in *Procedure*.

The separation by cation-exchange has been reported by Kuroda, Nakagomi and Ishida.[19] Most anions and metal ions listed in Table II can be separated effectively from scandium, except thorium and beryllium, which, however, are easily separated on the anion-exchange column (II).[20] The volume of effluent from column (II) is large, so the scandium should be concentrated before the photometric determination. The iron(III) hydroxide precipitate carries the scandium quantitatively from the sulphate solution. Anion-exchange column (III) serves as a trap for iron(III), yielding a good separation of scandium and iron.

The procedure described was applied to several types of rock samples. The results are quoted in Table III. Errors quoted are standard deviations. For comparison the values obtained by an arsenazo method previously reported[21] are also listed for the same three samples. There are no significant differences between the averages obtained by both methods. The Bromopyrogallol Red method is sufficiently sensitive to be applied to silicic rocks less abundant in scandium without large amounts of sample being needed.

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Zusammenfassung—Es wird eine hochempfindliche spektrophotometrische Methode zur Bestimmung von Scandium mit Brompyrogallolrot beschrieben; Mikrogrammengen Scandium können durch Messung bei 610 nm und pH 6,1 bestimmt werden. Der molare Extinktionskoeffizient beträgt $2{,}4 \cdot 10^4$ bei 610 nm. Die Bildung eines 1:1-Komplexes von Scandium mit Brompyrogallolrot wird bestätigt. Die normalerweise vorkommenden Kationen stören, können aber durch drei aufeinanderfolgende Ionenaustausch-Schritte vollständig abgetrennt werden, sodaß die Methode zur Bestimmung von Scandiumspuren in Silikatgesteinen angewandt werden kann. Es werden Ergebnisse von Scandiumbestimmungen in verschiedenen Arten von vulkanischen Gesteinen angegeben.

Résumé—On décrit une méthode spectrophotométrique hautement sensible pour doser le scandium au Rouge de Bromopyrogallol; on peut doser des quantités de scandium de l'ordre du microgramme par mesure à 610 mμ et pH 6,1. Le coefficient d'absorption moléculaire est de $2{,}4 \times 10^4$ à 610 mμ. On confirme la formation d'un complexe 1:1 du scandium avec le Rouge de Bromopyrogallol. Les cations communs gênent mais peuvent être complètement séparés par trois étapes successives d'échange d'ions, de sorte que la méthode peut être appliquée au dosage de traces de scandium dans les roches aux silicates. On note des résultats pour le scandium dans différentes roches ignées.

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STUDY OF BERYLLIUM OXINATE BY THE HOMOGENEOUS PRECIPITATION METHOD

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Summary—Beryllium oxinate has been precipitated from homogeneous solutions and the nature of the complex has been studied by thermogravimetric, infrared and X-ray methods. A structural formula has been proposed on the basis of the results.

THERE is controversy regarding the formation of the beryllium oxinate complex. Niessner,[1] from the reported quantitative separation[2] of aluminium from beryllium concluded that beryllium forms no complex with oxine. Rao *et al.*[3] reported precipitation of beryllium from aqueous solutions as the insoluble complex for which they gave the formula $Be(C_9H_6NO)_2$. On the other hand, Motojima[4] proposed the formula $Be_2O(C_9H_6NO)_2 \cdot 2H_2O$ for the complex he obtained. In a recent paper Magee and Gordon[5] pointed out that if a minimum radius ratio of 0·225 is the lower limit for a tetrahedral metal oxinate structure then ions of radius less than 0·32 Å would not be expected to form oxinates, so beryllium, with an ionic radius 0·31 Å, might be expected not to form a complex with oxine.

A detailed study on the formation of the beryllium oxinate complex was therefore undertaken. As precipitation from homogeneous solution is expected to give relatively pure compounds, this technique was used for the precipitation of the complex, which was then examined by thermogravimetric and infrared methods.

EXPERIMENTAL

Reagents

Beryllium nitrate solution was prepared from analytical grade material and standardized by the gravimetric ammonia method. The following solutions were also prepared from analytical grade reagents.

5% Oxine in acetone.
10% Urea in water.
10% Ammonium chloride in water.
0·1*N* Standard potassium bromate–potassium bromide mixture.
1% Triethanolamine (w/v) in water.

Apparatus

Cambridge pH-meter.

Stanton Model TR-1 thermobalance with sensitivity 1 mg, chart speed 6 in/hr, heating rate 4°/min.

Phillips 114·6-mm X-ray camera, with CuKα radiation.

Procedure for precipitation of the complex

Metal oxinates may be precipitated from homogeneous solution by three methods: (*a*) the urea hydrolysis method in which the pH of the solution is slowly raised until the desired pH is obtained;[6] (*b*) the mixed solvent method in which the mixture containing the metal and oxine dissolved in a solvent mixture such as acetone–water, adjusted to a predetermined pH, is slowly heated to 50–60° to volatilize the acetone with resulting gradual precipitation of the metal oxinate;[7] (*c*) the hydrolysis of 8-acetoxyquinoline to generate the reagent *in situ* for the precipitation of the complex.[8] Of these methods, only the first two methods are applicable in the case of beryllium, because in the third

method the acetic acid liberated either prevents the precipitation of beryllium oxinate or leads to low values.

Urea hydrolysis method. To a solution containing not more than 7·0 mg of beryllium are added 350 mg of oxine (7·0 ml of 5% solution), 500 mg of ammonium chloride and 4 g of urea. The volume of the solution is adjusted to 50 ml with distilled water. The solution is mixed thoroughly, and heated in a water-bath at 90°. Precipitation starts in 30–40 min (initial pH 3·5) and is complete in another 30–40 min. The precipitate is filtered off from the hot solution and washed with hot water followed by a few ml of acetone, and is then dried at 80° for 2 hr.

Mixed solvent method. To the solution containing not more than 9·0 mg of beryllium are added 7·0 ml of oxine solution, 25 ml of acetone and 10 ml of triethanolamine. The solution is mixed thoroughly, and heated on a water-bath at 60°. As the acetone evaporates, beryllium oxinate is slowly precipitated. At this stage the volume of the solution has been reduced to about 25 ml, and is diluted to 50 ml with hot water (80°). The temperature of the water-bath is now raised to 90° and maintained at this temperature until a clear orange yellow supernatant liquid is obtained (about 30 min). The precipitate is collected and dried as before.

Analysis of precipitates

The carbon and hydrogen contents of the precipitate were determined by microanalytical methods. The beryllium content was determined by igniting a known weight of the dried precipitate and weighing the beryllium oxide. The oxine content was estimated volumetrically with standard potassium bromate–potassium bromide solution. The values found were: C = 61·7%; H = 4·4%; Be = 4·96%; Oxine = 82·1%. Theoretical values for $Be(C_9H_6NO)_2$: C = 72·71%; H = 4·07%; Be = 3·03%; Oxine = 97·0%; for $Be_2O(C_9H_6NO)_2 \cdot 2H_2O$: C = 60·34%; H = 4·5%; Be = 5·03%; Oxine = 81·0%.

The molecular weight could not be determined by the conventional methods because of the insolubility of the precipitate in any of the common organic solvents.

RESULTS AND DISCUSSION

The beryllium oxinate precipitate obtained by either of the procedures described is a bright yellow crystalline solid and conforms to the formula suggested by Motojima[4] but not to the formula suggested by Rao *et al.*[3] The precipitate is insoluble in any of the common organic solvents—chloroform, acetone or alcohol, and exhibits a bright yellow fluorescence under ultraviolet light. The complex melts with decomposition at 290 ± 2°.

At least twice the theoretical amount of oxine is necessary for the precipitation of the complex. In the case of urea hydrolysis the precipitation starts at a pH of 5·5–6·0 and is complete at pH 7·0, whereas in the case of the mixed solvent method the final pH lies in the region 7·5–8·0. The interference of acetic acid and the need for a large excess of the reagent for the precipitation of the complex were probably responsible for the observation of earlier workers that beryllium forms no complex with oxine.

Pyrolysis of precipitate

When the complex is heated in an ignition tube, it melts, forming a brown to yellow-red solution, and needle-shaped crystals condense on the cooler parts of the tube along with some droplets of water. These crystals melt sharply at 76°, which corresponds to the melting point of oxine. This indicates that water and oxine are liberated from the complex on heating.

The differential thermogravimetric curve (Fig. 1) of the complex dried to constant weight at 80° indicates that the complex is stable up to 180° with three prominent regions of weight loss at 300°, 400° and 570°. In addition, a slow but significant weight loss occurs in the region 180–270° preceding the peak 300°. The decomposition is complete at 690° with no subsequent weight loss.

The loss in the region 180–270° corresponds to one molecule of water; the total

loss after ignition is 86·9%, giving the value for the loss of oxine (complete volatilization) as 81·9%. This agrees reasonably with the theoretical value for the oxine content. However, only one water molecule is accounted for (the total loss up to 300°, corresponding to the first peak, is more than that required for two molecules of water). It may be recalled that Charles,[9] in his studies with barium oxinate tetrahydrate, observed

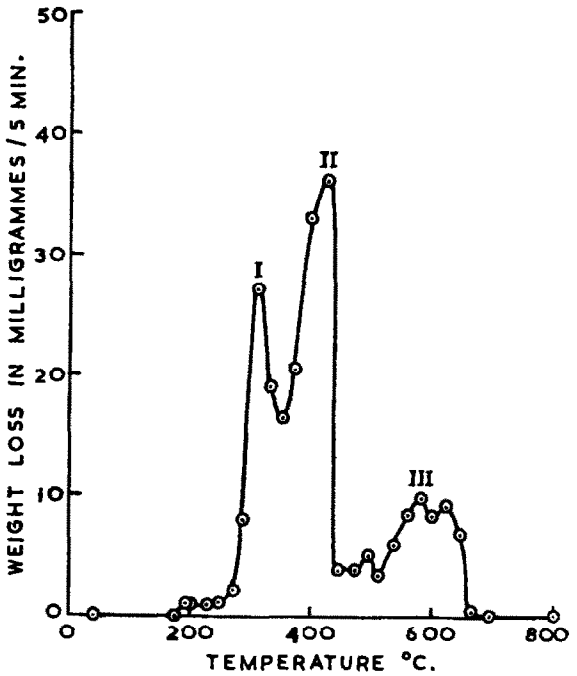


FIG. 1.—Differential thermogravimetric curve of the oxinate obtained by PFHS.

that oxine was liberated during pyrolysis, and his pyrolysis data accounted for only two molecules of water. This was explained as arising from solid-state hydrolysis of the complex.

The pyrolysis of beryllium oxinate can also be explained similarly. The loss of weight up to 270° arises from the loss of one molecule of water from the compound:

$$Be_2O(C_9H_6NO)_2{\cdot}2H_2O \rightarrow \underset{(A)}{Be_2O(C_9H_6NO)_2{\cdot}H_2O} + H_2O. \qquad (1)$$

The high temperature required for this reaction (180–270°) indicates that the water is strongly bound.

The compound *A* thus formed is unstable, as the co-ordination sphere of beryllium is disturbed, and solid-state hydrolysis occurs according to the equation

$$Be_2O(C_9H_6NO)_2{\cdot}H_2O \rightarrow \underset{(B)}{Be_2O(C_9H_6NO)OH} + C_9H_7NO. \qquad (2)$$

The intermediate compound *B* formed is very unstable and decomposes rapidly according to the reaction:

$$Be_2O(C_9H_6NO)OH \rightarrow 2BeO + \text{oxine(decomposed)}. \qquad (3)$$

Peak I thus arises from reaction (2), where the oxine liberated is volatilized. Peak II represents the reaction (3) where the intermediate compound *B* decomposes. However, these reactions could not be assessed quantitatively as the peaks overlap and the intermediate compounds cannot be isolated because of their high instability, as indicated by the position of the trough on the differential curve.[10] Peak III consequently represents the oxidation of carbonaceous matter formed during the decomposition of the precipitate.

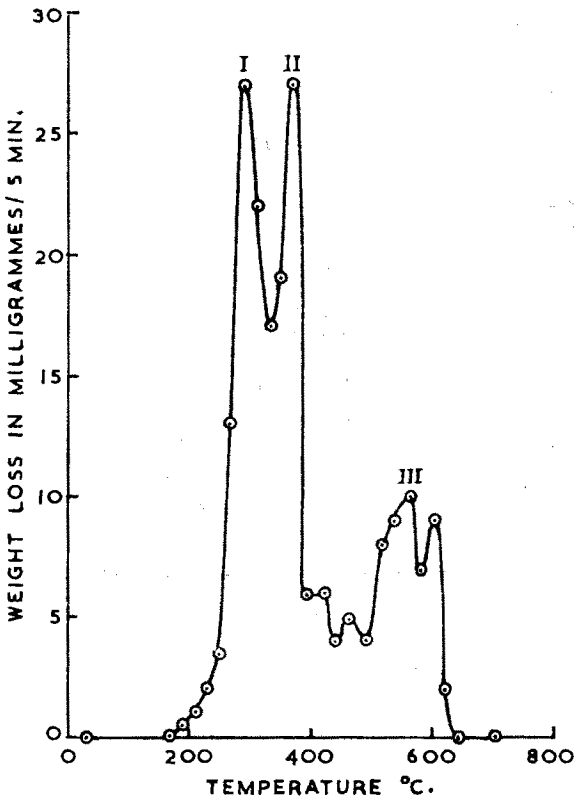


FIG. 2.—Differential thermogravimetric curve of the oxinate obtained by Motojima's method.

From the foregoing discussion it is evident that the beryllium oxinate precipitated from homogeneous solution has the same molecular formula as that suggested by Motojima.[4] This is further illustrated by the differential curve of the compound prepared according to the procedure suggested by him (Fig. 2) and dried at 80°.

Infrared study

The infrared spectrum of the complex is given in Fig. 3. The infrared spectra of oxinates are generally similar having a characteristic peak[11] around 1100 cm^{-1}. In the case of beryllium oxinate this peak occurs at 1108 cm^{-1}. The absence of the peak at 710 cm^{-1} characteristic of the oxine indicates the absence of free oxine in the complex.

The spectrum of beryllium oxinate shows strong bands in the 1000–790 cm^{-1} region, indicating that the metal–oxygen bond is strong and that the water molecules form

strong co-ordination bonds with beryllium.[12] The spectrum also shows bands at 3600 cm^{-1} (OH-stretching of water) and 1600 cm^{-1} (H—O—H bending) which are to be expected on the basis of the suggested formula.

In addition, the spectrum shows a characteristic absorption at 946 cm^{-1}. Such characteristic absorptions were also noted in the case of a few other oxinate complexes of metals. Thus Charles *et al.*[11] found that uranyl oxinate has a characteristic peak

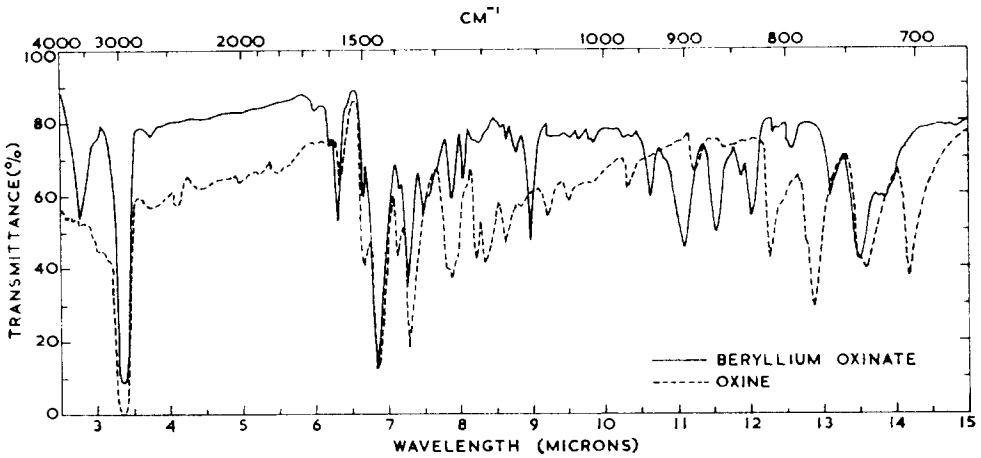


FIG. 3.—Infrared spectrum of the oxinate.

at 892 cm^{-1} and assigned it to the UO_2 group. Magee and Martin[13] found that niobium and tantalum oxinates exhibit characteristic peaks at 921, 914 and 904 cm^{-1}. The niobium peak at 921 cm^{-1} was attributed by them to the NbO group. Assuming that the tantalum peak at 914 cm^{-1} is due to the TaO group, the 927 cm^{-1} peak[13] of molybdenum to the MoO_2 group and the 946 cm^{-1} peak of beryllium to the BeO group, a straight-line relation is obtained when the peak position in the 10·5-μ region is plotted against the first ionization potential of the metal (Fig. 4); the peak position is expressed in microns for convenience. It is interesting to note that Be, Nb, Ta, U, and Mo, the complexes of which contain Be_2O, NbO, TaO, UO_2 and MoO_2, fall very nearly on a straight line while Co and Mn, whose oxinates do not have metal–oxygen linkages, fall outside it.

X-ray examination

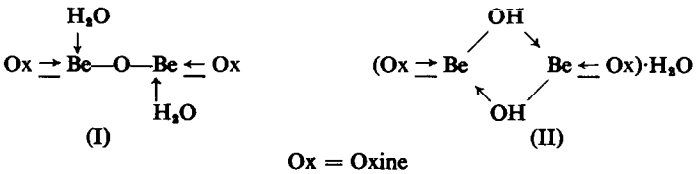
X-ray examination showed that the beryllium oxinate complex is orthorhombic with the unit cell dimensions $a = 9{\cdot}42$ Å, $b = 12{\cdot}5$ Å and $c = 14{\cdot}32$ Å. The density measured by weighing in air and in benzene is 1·361 g/cm^3. The density calculated for 4 molecules of $Be_2O(C_9H_6ON)_2{\cdot}2H_2O$ per unit cell is 1·409 g/cm^3.

Analytical applications

The procedures described for the precipitation of the beryllium oxinate complex have been found to give excellent values for the gravimetric determination of beryllium in the 1·5–9·0 mg range.

Conclusion

These studies clearly show that beryllium forms a complex of well defined composition, $Be_2O(C_9H_6NO)_2 \cdot 2H_2O$. Two structural formulae are possible for this compound:



Ox = Oxine

Evidence for the existence of beryllium compounds containing hydroxyl bridges[14] and the preferential removal of one molecule of water during pyrolysis lend support for structure II. However, the fact that the complex is stable up to 180° and that the loss of water occurs over a wide range of temperature (heating the compound at 160° for

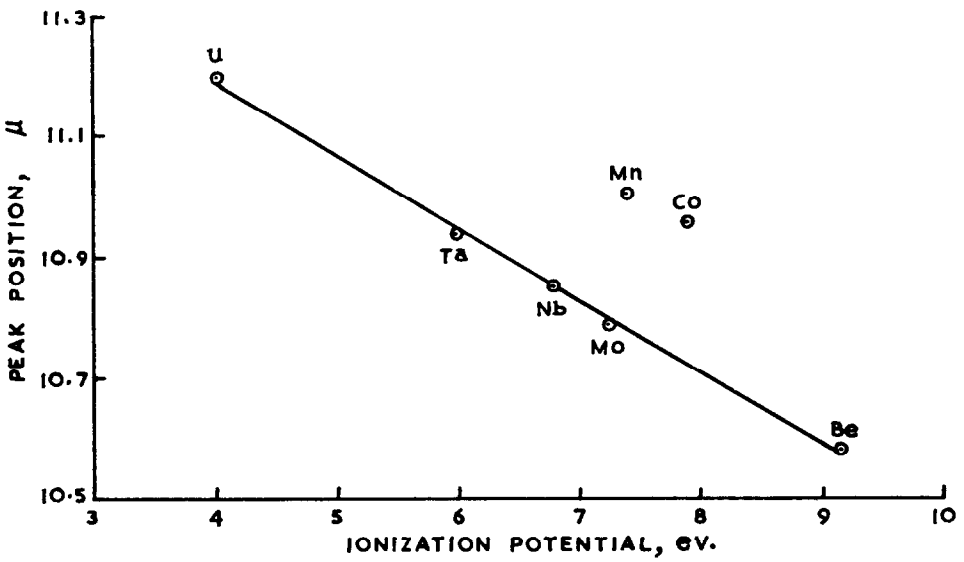


FIG. 4.—Relation between peak position (in the 10–11 μ region) *vs.* first ionization potential of the metal.

2 hr resulted in less than 2% weight loss) shows that the water present is more strongly bound than lattice water. It may further be seen that the liberation of oxine (Peak I) occurs immediately after the loss of one molecule of water without a complex being formed that is free from lattice water, as normally expected. This can be explained if water is present in the co-ordination sphere, which will be disturbed with consequent decomposition when the water is removed. The bands in the region 1000–790 cm^{-1} in addition to those at 3600 cm^{-1} (OH-stretching) and 1600 cm^{-1} (H—O—H bending) which are assigned to the wagging, rocking and twisting motions of water present in the coordination sphere[12] are clearly indicated in the infrared spectrum. The available evidence therefore appears to favour structure I.

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Technology, Kanpur, India for useful suggestions on the infrared spectra and Professors M. R. A. Rao and A. R. V. Murty, Indian Institute of Science, Bangalore, India for providing facilities for the X-ray work.

Zusammenfassung—Berylliumoxinat wurde aus homogenen Lösungen gefällt und die Natur des Komplexes durch thermogravimetrische, Infrarot- und Röntgenmethoden untersucht. Auf Grund der Ergebnisse wird eine Strukturformel vorgeschlagen.

Résumé—On a précipité l'oxinate de beryllium à partir de solutions homogènes et étudié la nature du complexe par les méthodes thermogravimétrique, infra-rouge et aux rayons X. On propose une formule développée sur la base de ces résultats.

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APPLICATION OF RADIOISOTOPES IN COLUMN CHROMATOGRAPHY ON SUBSTITUTED CELLULOSES—VI*

THE SEPARATION OF ANTIMONY FROM MANGANESE, IRON AND OTHER METALS

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Summary—The chromatographic behaviour of nanogram amounts of antimony in ethyl ether medium was studied by radioisotope techniques on cellobiose, cellulose and seven substituted celluloses. It was found that antimony is strongly retained and can be separated from macro amounts of manganese, iron, gold, uranium, mercury, arsenic and several other metals. Antimony could be quantitatively recovered by elution from natural cellulose and cellobiose. The method can be applied in several analytical problems concerning the separation of traces of antimony.

INFORMATION on the chromatographic behaviour of antimony on natural cellulose was first given when uranyl nitrate was purified from numerous trace elements by chromatography: it was observed that antimony was retained on a cellulose column.[1] Traces of antimony have been eluted from a cellulose column by means of a mixture of acetone and concentrated hydrochloric acid after the separation of large amounts of uranium,[2] and antimony has been separated from germanium and eluted from a narrow column of natural cellulose.[3]

One of the most important separations of small amounts of antimony from a matrix is that of antimony from cast iron. This has been done by co-precipitation of antimony on manganese dioxide formed from permanganate and manganese(II);[4] several ions interfere, particularly iron(III). The antimony separated must then be determined by those methods with which manganese does not interfere. Practically the same method has been recently applied to the determination of traces of antimony in marine water, but the antimony was subsequently separated from manganese and interfering elements by solvent extraction.[5] More recently antimony has been separated by isotopic exchange.[6] The influence of iron, manganese and arsenic was not examined, and the method was limited to a narrow range of amounts of metals, required addition of antimony as carrier, and was subject to several interferences.

A method which offered a rapid separation of antimony from iron and other metals, with few interferences, and which allowed recovery of traces of antimony without chemical or isotopic dilution would be more widely applicable.

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The strong retention of antimony on natural cellulose[2] indicated that it was possible to separate traces of antimony from a number of elements. Natural and substituted celluloses have been examined to establish which metals disturb the retention of antimony, and to find the best conditions of quantitative elution.

EXPERIMENTAL

Solutions

Reagent-grade chemicals and solvents were used for the preparation of all solutions, without further treatment. The following solutions were prepared:

(*a*) anhydrous ethyl ether
(*b*) 2 ml of 90% nitric acid in 98 ml of ethyl ether
(*c*) 40 mg of ammonium thiocyanate in 20 ml of methanol plus 80 ml of ethyl ether
(*d*) 5 g of ammonium thiocyanate in 20 ml of methanol plus 80 ml of ethyl ether.

Concentrated hydrochloric acid, 0·5, 1·5 and 5*M* in methanol.
Aqueous nitric acid, 0·5, 1·5 and 5*M*.
Solutions (5% w/v) of iron(III) chloride hexahydrate, mercury(II) chloride and chloroauric acid trihydrate in solution (*b*).

Celluloses

Cellulose Whatman CF 11, powder, natural.
Cellulose Whatman DE 11, powder, diethylaminoethyl.
Cellulose Whatman AE 11, powder, aminoethyl.
Cellulose Whatman P 11, powder, phosphate.
Cellulose Whatman CM 11, powder, carboxymethyl.
Cellulose Whatman ET 11, powder, epichlorohydrin triethanolamine, Ecteola.
Cellobiose Sigma CB, powder, (glucose-β-glucoside).
Cellulose Bio-Rad SE, powder, sulphoethyl.
Cellulose Bio-Rad PAB, powder, para-aminobenzyl.

Radioisotopes

Antimony-125 solution, carrier-free, was provided by New England Nuclear Corp., Boston, Mass., U.S.A. Its concentration was ~0·3 mg/ml and 10 μl of it were diluted with 10 ml of 90% nitric acid. Aliquots of 100 μl of this solution, corresponding to 30 mg of antimony, were used for each experiment.

The other radioisotopes used are listed in earlier parts of this series.[7–9]

Procedures

The eluted aliquots and the cellulose powders were collected in plastic bottles of uniform shape and capacity. Their radioactivity was measured by a 128-channel gamma-ray spectrometer, ND-110, electronically coupled to an NaI(Tl) crystal, and compared with a standard. The average deviation of results was 8%.

The columns (15 × 1 cm; Teflon stop-cock) were prepared as described earlier[7,8] and operated under pressure to give a flow-rate of about 20 ml/min. The time needed for preparing two columns and doing two complete runs was one hour.

RESULTS AND DISCUSSION

All the celluloses examined collect antimony from ether–nitric acid mixtures, and further washing with this solution is without eluting effect.

Solutions (*c*) and (*d*) do not elute antimony, nor does a 2% solution of potassium hydrogen tartrate. A solution of oxalic acid in 0·5*M* hydrochloric acid gives the same elution curves as 0·5*M* hydrochloric acid alone.

Solutions of hydrochloric acid in methanol and of nitric acid in water elute antimony; pure water and pure methanol do not, so the acids are the necessary eluting agents. Aqueous hydrochloric acid is also convenient but the methanol solutions cause less swelling of the celluloses, though a slight applied pressure is needed.

Table I shows the extent of elution of antimony from natural and substituted celluloses with aqueous nitric acid. Cellulose phosphate very strongly retains antimony and there is little elution. There is a remarkable similarity in the elution of antimony from amino-celluloses and from natural cellulose. The amino-substituted celluloses were decolorized when treated with dilute nitric acid, suggesting that the amino groups were probably destroyed and the properties of these celluloses were altered. Antimony was quantitatively recovered from Ecteola cellulose.

TABLE I.—ELUTION OF ANTIMONY FROM VARIOUS CELLULOSES BY NITRIC ACID*

Fraction number†	Eluent	Antimony in fraction, % Celluloses					
		CF	DE	AE	CM	P	ET
16		35	50	62	30	12	60
17	0·5*M* HNO_3	10	20	5	31	3	17
18		5	7	3	5	2	3
19		7	3	5	5	5	3
20	1·5*M* HNO_3	5	2	—	6	—	3
21		10	3	10	10	—	7
22	5*M* HNO_3	8	4	4	7	2	8
23		5	—	2	—	—	3
Column		15	15	7	13	76	4
Total		100	104	98	107	100	108

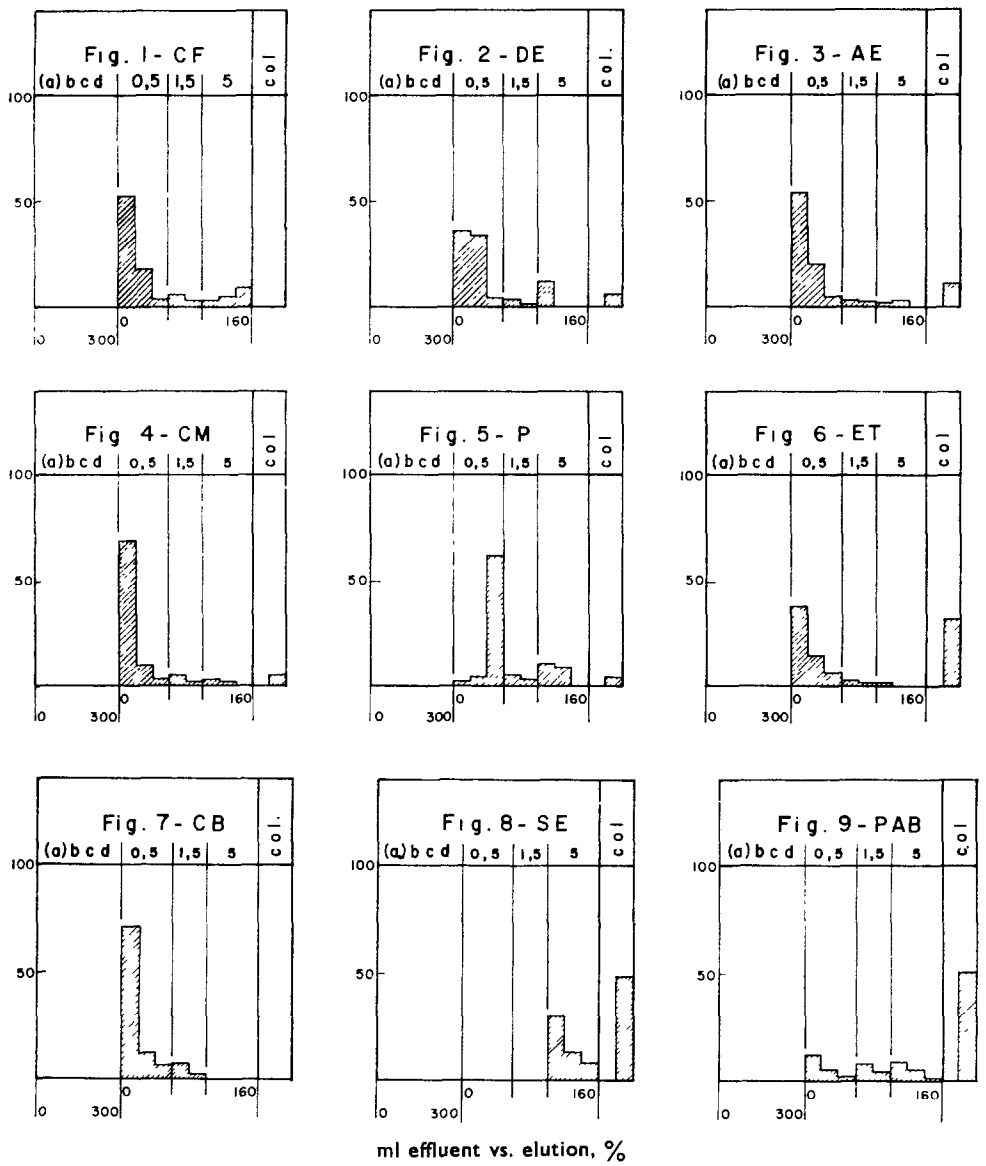
* After passage of 100 ml each of solutions (*a*), (*b*) and (*c*).
† 20-ml fractions.

The elution of antimony with hydrochloric acid in methanol is shown in Figs. 1–9, and is generally delayed for the substituted celluloses relative to the elution from natural cellulose, particularly for cellulose phosphate and the amino-substituted celluloses, confirming the general trend that substituted celluloses adsorb cations more strongly than natural cellulose does.

Antimony was completely recovered from natural cellulose, and in yields varying from 90 to 96% from the substituted celluloses except for ET, SE and PAB celluloses where 32%, 50% and 42% of antimony respectively were still retained after passage of the eluting solutions.

Because natural cellulose allows the most complete elution of antimony and retains transition metals relatively less strongly than substituted celluloses, it was used for examining the possible separation of antimony from other metals. Traces of antimony were separated from traces of iron on natural cellulose: ethyl ether containing traces of iron and antimony was passed at a high flow-rate through the column and both metal ions remained at the top. Iron was subsequently eluted with diluted thiocyanate solution (*c*) and antimony was eluted with hydrochloric acid (Fig. 10) Comparison of Figs. 3, 4 and 6 with Figs. 3, 4 and 6 of Part III of this series[8] shows that this separation can also be done on AE, CM, ET, SE and PAB celluloses, even though the elution of antimony would not be quantitative.

Antimony was also separated on CF cellulose from nanograms of silver, zinc, chromium and cobalt and from micrograms of manganese, all of which were eluted



FIGS. 1–9.—The chromatographic behaviour of 30 nanograms of antimony on natural and substituted celluloses and cellobiose in ethyl ether-nitric acid mixture, eluted with 0·5, 1·5 and 5*M* hydrochloric acid in methanol.

with solution (*c*),[8] and from copper.[9] Nanogram amounts of antimony were also separated from mercuric chloride, chloroauric acid and uranyl nitrate, gram amounts of which did not affect the adsorption of the antimony on cellulose. The small amounts of these retained by the column could be washed off with solutions (*a*) or (*b*). Similar results were obtained with gram amounts of iron(III) chloride, the excess of which passed through the column, and the retained fraction was eluted with thiocyanate solution. Thiocyanate was then washed off the column with methanol and antimony was quantitatively eluted as described. The same procedure

could be applied to macro amounts of the other elements mentioned, the limiting factor being the solubility of their nitrates or chlorides in ethyl ether.

It is noteworthy that large quantities of chloroauric acid and of the other chlorides used do not elute antimony, even though hydrochloric acid does.

CONCLUSIONS

Antimony is very strongly adsorbed on natural cellulose, and even more strongly on substituted celluloses, particularly cellulose phosphate. Arsenic is not adsorbed on celluloses from ether-nitric acid mixture,[9] though bismuth is retained and generally can be eluted with thiocyanate solutions. There is no progressive variation of chromatographic behaviour within Group VA and no physico-chemical parameter can be found at present to explain this.

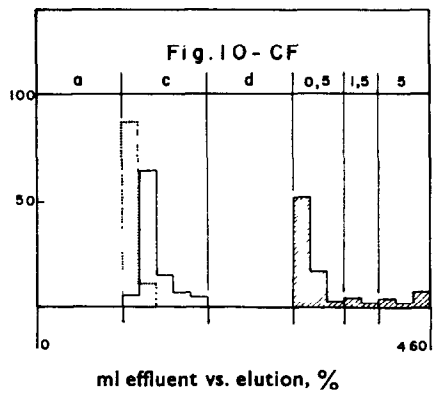


FIG. 10.—The chromatographic separation of 30 nanograms of antimony (shaded area) from gram amounts of iron (. . . .) and manganese (—) on natural cellulose.

As only a few other elements are strongly adsorbed, *e.g.*, barium and caesium,[2] antimony can be separated from a large number of elements by chromatography on any convenient cellulose.

The separations reported here can be applied in several important analytical problems: adsorption chromatography on columns of cellulose is easy and rapid to perform, is practically independent of certain parameters such as temperature, and large samples can be treated and purified.

Acknowledgement—This research was conducted under Grant No A-2507 attributed by the National Research Council of Canada to R. A. A. Muzzarelli who gratefully expresses his appreciation.

Résumé—Le comportement chromatographique de nanogrammes d'antimoine en éther éthylique a été étudié à l'aide de radioisotopes sur cellobiose, cellulose et sept celluloses substituées; il a été trouvé que l'antimoine est fortement adsorbé et peut être séparé d'avec quantités de l'ordre du gramme de manganèse, fer, or, uranium, mercure, arsenic et quelques autres éléments. L'antimoine pût être élué quantitivement de la cellulose naturelle et du cellobiose. La méthode est applicable à certains problèmes de chimie analytique concernant les traces d'antimoine.

Zusammenfassung—Chromatographischen Verhalten von Nanogrammenge Antimon an der Cellobiosesäule, Cellulosesäule und sieben modifizierten Cellulosesäulen wurde mit Radioisotoptechnik untersucht. Antimon ist sehr stark adsorbiert und deshalb konnte ohne Schwierigkeiten von Grammengen Gold, Eisen, Mangan, Uranium, Quecksilber, Arsen, und von anderen Metallen abgetrent werden. Antimon wurde von der natürliche Cellulose und Cellobiose vollständig ausgespült. Diese Methode kann man für Antimonspurenbestimmung in analytischen Chemie angewendet werden.

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EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM(V) WITH 8-HYDROXYQUINOLINE

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Summary—The extraction and spectrophotometric determination of vanadium (V) with oxine is investigated at higher acidities than described previously. Under these conditions, n-butanol and other alcohols are found to exert a synergic effect on the extraction of vanadium into benzene. In the presence of alcohol only a 6-fold ligand excess is needed for quantitative extraction in a single operation, the acidity of the aqueous medium being 0·05*M* with respect to sulphuric or phosphoric acid. The interference of iron(III) in the spectrophotometric determination of vanadium is suppressed by the addition of pyrophosphate. Beer's law is obeyed up to 14·0 μg of vanadium/ml and the sensitivity is 0·008 μg of vanadium/cm^2 at 390 mμ. The composition of the extracted species is found to be vanadium:oxine:n-butanol = 1:2:2.

SEVERAL authors have investigated the separation and photometric determination of vanadium(V) based on the extraction of the blue-black complex of vanadium(V) with oxine, formed at pH 3–5, into organic solvents such as chloroform,[1–7] benzene,[8] carbon tetrachloride,[9] isoamyl alcohol,[10–12] amyl acetate[11,12] and chlorohydrocarbons.[13] These methods require repeated extractions for quantitative recovery, complicated and sometimes cumbersome operations for the elimination of the interference of foreign ions, notably iron(III), a lengthy equilibration, a narrow range of pH and a high concentration of the ligand. Further, no thorough investigation has been made of the nature and composition of the extracted species.

The procedure described below allows the rapid separation and determination of vanadium and offers several advantages in that almost quantitative recovery (average 99·1 %) of vanadium can be achieved in a single extraction even with a 1-min equilibration. A 6-fold excess of ligand is sufficient for quantitative extraction and the colour of the organic phase is quite stable.

EXPERIMENTAL

Apparatus

The absorbance measurements were made on a Beckman Model DU spectrophotometer, in 1-cm Corex cells.

Reagents

Oxine solution. Analytical reagent grade (B.D.H.) 8-hydroxyquinoline dissolved in analytical reagent grade (thiophene-free) benzene.

Vanadium(V) solution, 0·01*M*. Guaranteed reagent grade (Merck) ammonium metavanadate dissolved in doubly distilled water, and standardized with standard iron(II) solution.

n-Butanol and other alcohols were purified by distillation. All other chemicals used were of analytical reagent grade.

Procedure for investigation of the extraction

Equilibrate 25·0 ml of an aqueous solution of vanadium(V) at the required acidity for 1 min with 25·0 ml of the solvent containing the requisite amount of oxine. Separate the phases and reduce the

vanadium(V) in the organic phase to vanadium(IV) by shaking it with sulphite solution in the presence of 1·0*M* sulphuric acid and back-extract into water. Oxidize the vanadium(IV) to vanadium(V) with permanganate and titrate it potentiometrically with iron(II) solution.[14]

Effect of acidity

Favourable extraction is achieved from sulphuric and phosphoric acid media. The results in Table I show the extraction of vanadium(V) into benzene from both these media at various acidities, in the presence and absence of n-butanol.

TABLE I.—EFFECT OF ACIDITY

Acidity, *M*	Extraction, %			
	Sulphuric acid		Phosphoric acid	
	20% n-Butanol in benzene	Pure benzene	20% n-Butanol in benzene	Pure benzene
0·005	98·8	84·1	37·5	37·5
0·050	98·9	47·8	99·0	72·4
0·125	60·4	5·5	98·4	60·5
0·250	29·1	nil	94·7	24·5
0·500	11·7	nil	64·3	nil
1·000	nil	nil	16·6	nil

Aqueous phase contains 50 μmole of vanadium(V).
Organic phase contains 500 μmole of oxine.

Quantitative recovery is achieved from 0·005–0·05*M* sulphuric acid and 0·05–0·125*M* phosphoric acid. Alcohol exerts a synergic effect on the extraction.

Effect of the concentration of n-butanol in the organic phase

For quantitative recovery of vanadium with benzene, the organic phase should contain 20% of n-butanol, the acidity of the aqueous phase being 0·05*M* with respect to either sulphuric or phosphoric acid. Other alcohols such as n-amyl alcohol and benzyl alcohol behave similarly.

Effect of oxine concentration

Table II gives the results of the study of the effect of oxine concentration on the extraction into pure benzene and into benzene containing 20% of n-butanol. Whereas in the presence of n-butanol,

TABLE II.—EFFECT OF OXINE CONCENTRATION

[Oxine] / [Vanadium(V)]	Extraction, %	
	Benzene	20% n-Butanol in benzene
1	nil	20·8
5	9·0	90·0
6	20·0	98·9
10	47·8	98·9
30	93·9	98·9
40	97·5	98·9
50	97·8	98·9
60	97·8	98·9

Aqueous phase—0·05*M* with respect to sulphuric acid, and containing 50 μmole of vanadium(V).

only a 6-fold excess of ligand is needed to give quantitative recovery, a 50-fold excess is needed with pure benzene as solvent.

Effect of time of equilibration and volume of the organic phase

Maximum extraction is achieved even with 1 min equilibration provided equal volumes of aqueous and organic phases are used. If the volume of the organic phase is less than that of the aqueous phase, the degree of extraction is reduced.

Procedure for spectrophotometric determination

Mix an aliquot of vanadium(V) solution containing up to 14·0 μg of vanadium/ml with enough sulphuric or phosphoric acid to give an overall acidity of 0·05*M* on dilution to 25·0 ml with redistilled water. Add 5·0 ml of 0·1*M* oxine solution in benzene, 5·0 ml of n-butanol and 15·0 ml of benzene,

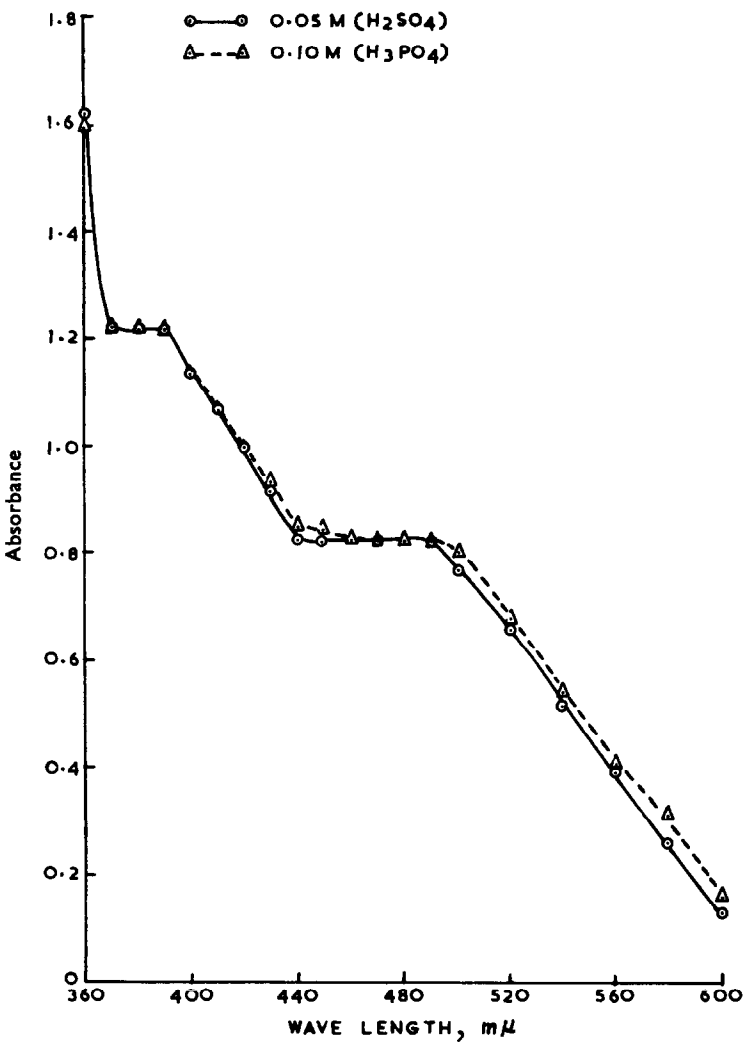

FIG. 1.—Absorption spectrum of vanadium(V)–oxine complex extracted into 20% n-butanol in benzene.
Vanadium(V) = 2·0 × 10^{-4}*M*.

and shake for 1 min. Separate the organic phase, dry it over anhydrous sodium sulphate, and measure its absorbance at either 390 mμ or 480 mμ against 20% n-butanol solution in benzene.

The absorption spectra of the red vanadium(V)–oxine complex extracted from 0·05*M* sulphuric and 0·10*M* phosphoric acids into 20% n-butanol solution in benzene are given in Fig. 1. They are

similar to those obtained by earlier workers[13,15] under different experimental conditions. Identical spectra are obtained with other alcohols such as n-amyl alcohol or methanol in place of n-butanol. The red colour is stable for more than 6 hr whereas the colour of the extract in the absence of any alcohol fades very rapidly, indicating that the complex decomposes. The recovery of vanadium is shown in Table III.

TABLE III.—RECOVERY OF VANADIUM

Vanadium(V) taken, *mmole*	Vanadium(V) recovered, %
0·025	98·5
0·050	98·7
0·075	99·0
0·100	99·2
0·125	99·5
0·150	99·5
0·200	99·2

Benzene phase contains 1·50 mmole of oxine and 20% of n-butanol.

Sensitivity of the colour reaction

The molar absorptivities at 390 and 480 mμ are $6{\cdot}02 \times 10^3$ and $3{\cdot}95 \times 10^3$ respectively, the sensitivities[16] being 0·008 μg and 0·013 μg of vanadium/cm^2 respectively at these wavelengths.

Interferences

Al, Be, Cd, Ce(III), Co(II), Cr(III), Mg, Mn(II), Ni, Th, U(VI), V(IV) and Zn, even when present in 1000-fold excess, are without effect on the extraction and photometric determination of vanadium(V). Although Cu(II), Mo(VI), and W(VI) give coloured extractable precipitates under the experimental conditions they do not interfere with the recovery of vanadium. In the photometric determination their tolerance limits are Cu(II) 0·6 mg, Mo(VI) 1·0 mg, and W(VI) 0·9 mg per 0·13 mg of vanadium. Fe(III) also gives an extractable coloured product but its interference is completely suppressed by addition of excess of pyrophosphate. Citrate, fluoride, pyrophosphate, phosphate and tartrate do not interfere but the extraction is markedly inhibited by oxalate and EDTA. Reagents which reduce vanadium(V) to lower oxidation states should be absent.

Composition of the extracted species

The composition of the extracted species is determined by plotting log (distribution ratio) *vs.* log (reagent concentration) in the presence and absence of alcohol. The amount of vanadium(V) taken in all the experiments was 50 μmole. It can be seen that in the absence of alcohol the ratio of vanadium(V) to oxine in the extracted species is 1:2 (Fig. 2). Even when the aqueous phase is 0·125*M* with respect to phosphoric acid, the same ratio is obtained. With a constant concentration of alcohol (20% v/v) in the organic phase the log (*D*) *vs.* log [oxine] curve (Fig. 3) shows two straight line portions with slopes of 1 and 2, indicating that at low concentrations of oxine the species contains vanadium and oxine in the ratio 1:1, and at higher concentrations the ratio is 1:2. With a constant concentration of oxine, (0·02*M* in the organic phase) the dependence of extraction on the concentration of n-butanol was investigated, the acidity of the aqueous phase being kept at 0·25*M* with respect to sulphuric acid. The log (*D*) *vs.* log [n-butanol] curve (Fig. 4) shows two straight line portions with slopes of 1 and 2 indicating the existence of a 1:1 vanadium:n-butanol species at low alcohol concentrations and a 1:2 species at high alcohol concentrations. Similar results are obtained for phosphoric acid medium, the acidity being 0·5*M*.

Job's method[17]

The method of continuous variations was adapted for the two phase system.[18] Equimolar solutions (0·01*M*) of vanadum(V) in the aqueous phase and of oxine in 20% n-butanol in benzene were prepared. These two solutions were mixed in such proportions that in each system the total concentration of vanadium(V) and oxine was the same ($4{\cdot}0 \times 10^{-3}M$) and the mole fraction of vanadium varied from 0–1·0, the aqueous phase being kept 0·05*M* in sulphuric acid or 0·25*M* in phosphoric acid. After equilibration for 1 min, the organic phase was separated and dried over anhydrous sodium sulphate,

and its absorbance was measured. The curves at 390 and 480 mμ are given in Fig. 5 and indicate that the extracted species from both acid media contain vanadium and oxine in a 1:2 ratio.

Slope-ratio method[18,19]

In this method, the concentration of one component was kept at $4{\cdot}0 \times 10^{-3}M$ while that of the other was varied from $1{\cdot}0 \times 10^{-4}M$ to $6{\cdot}0 \times 10^{-4}M$. The results are presented in Fig. 6 in which curves A_1 and B_1 refer to the absorbances at 390 and 480 mμ when the oxine concentration was kept constant, and A_2 and B_2 are the corresponding curves for a constant concentration of vanadium.

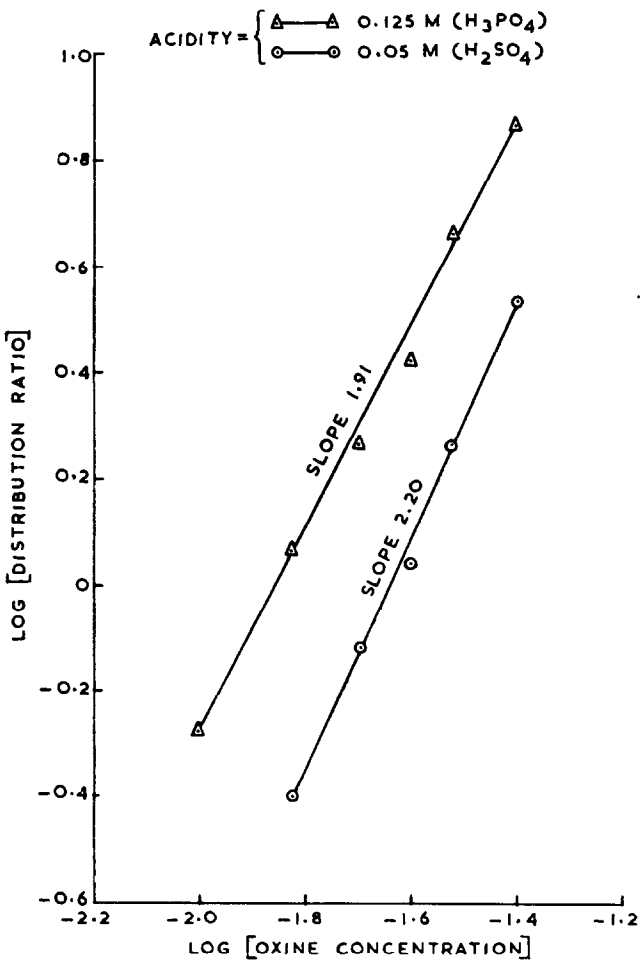

FIG. 2.—Nature of the vanadium(V)–oxine species extracted.

The slope-ratios A_1/A_2 and B_1/B_2 are 2·29 and 2·3 respectively, confirming that the mole ratio of vanadium:oxine in the species is 1:2. The same value is obtained when the extraction is carried out from an aqueous phase $0{\cdot}25M$ with respect to phosphoric acid.

DISCUSSION

Under the experimental conditions, vanadium(V) in solution exists as univalent VO_2^+.[20,21] Since only neutral species are extracted into organic solvents, it is probable that first a 1:1 chelate is formed between vanadium(V) and oxine. This chelate adds another oxine molecule by replacement of water, thus rendering it hydrophobic and

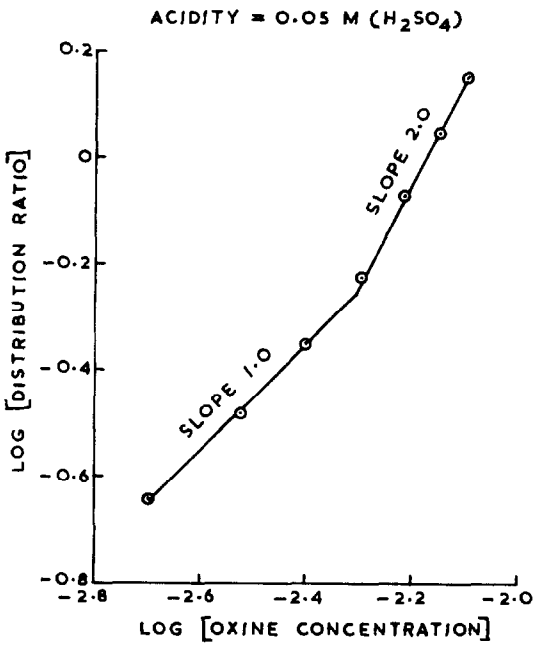

FIG. 3.—Nature of the extracted vanadium(V)–oxine–n-butanol species.

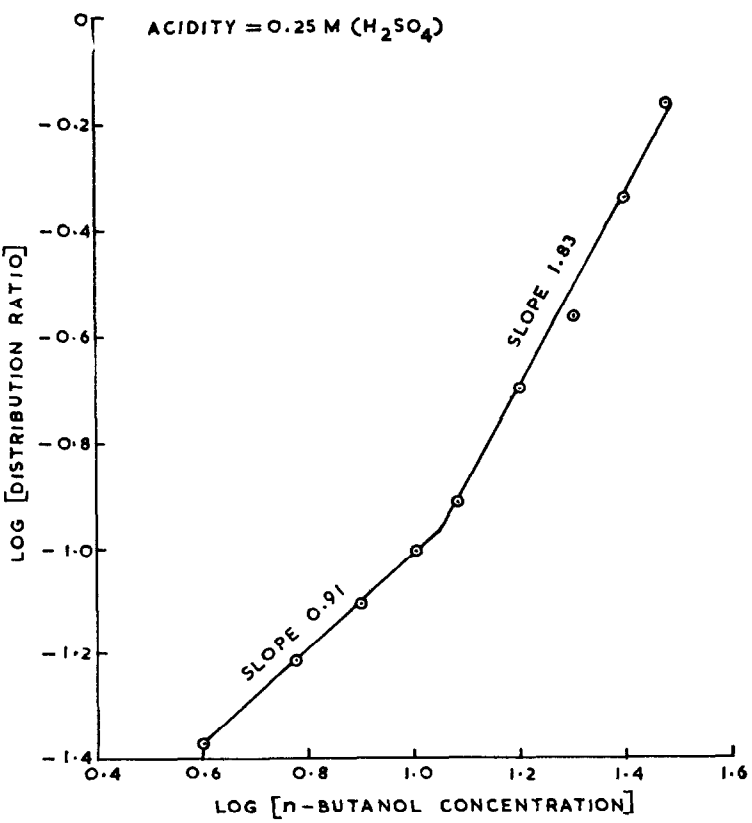

FIG. 4.—Nature of the vanadium(V)–oxine–n-butanol species extracted.

soluble in organic solvents as in the case of magnesium[22] and strontium.[23] This accounts for the fact that in the absence of alcohol no extraction is observed at very low concentrations of oxine where there is not enough oxine to form the adduct. However, recovery is quantitative when the concentration of oxine is about 50 times that of the vanadium and under these conditions the log-log plots indicate that the

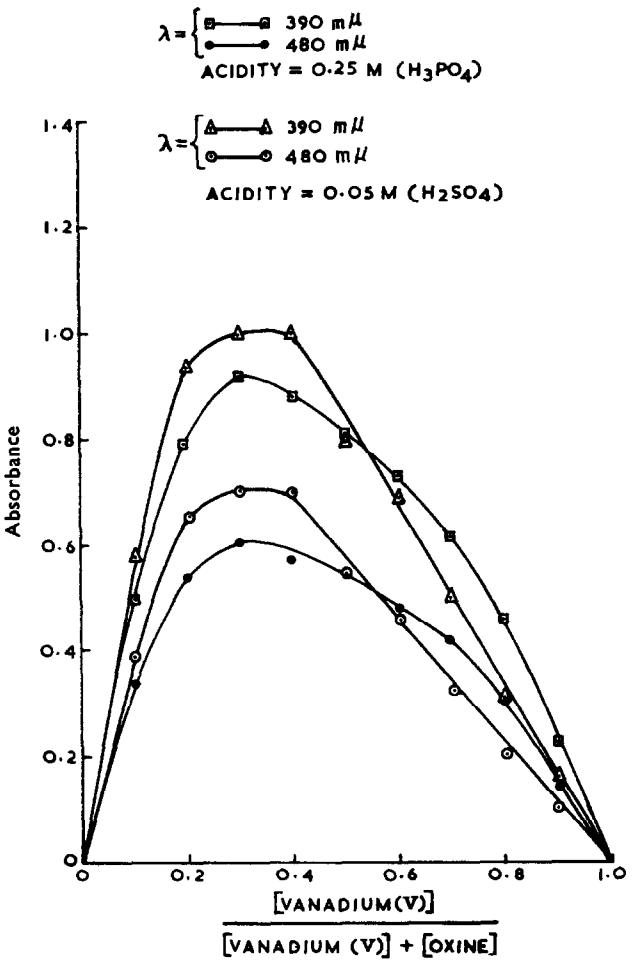

FIG. 5.—Nature of the vanadium(V)–oxine species extracted: Job's method.

composition of the extracted species is 1:2 vanadium:oxine (Fig. 2). However, in the presence of an alcohol, even at a low concentration of oxine, some recovery of vanadium is observed. Under these conditions evidence for a 1:1 vanadium:oxine species is given by the log–log plot, although at higher concentrations of oxine a 1:2 species is also indicated (Fig. 3). This explains the mechanism of the synergic effect of alcohol. The formation of a 1:2 vanadium:oxine species is also indicated by the spectrophotometric methods (Figs. 5 and 6). The log–log plot (Fig. 4) shows that either one or two molecules of n-butanol are associated with each species extracted, depending on the concentration of the n-butanol. In view of the fact that in routine extraction work,

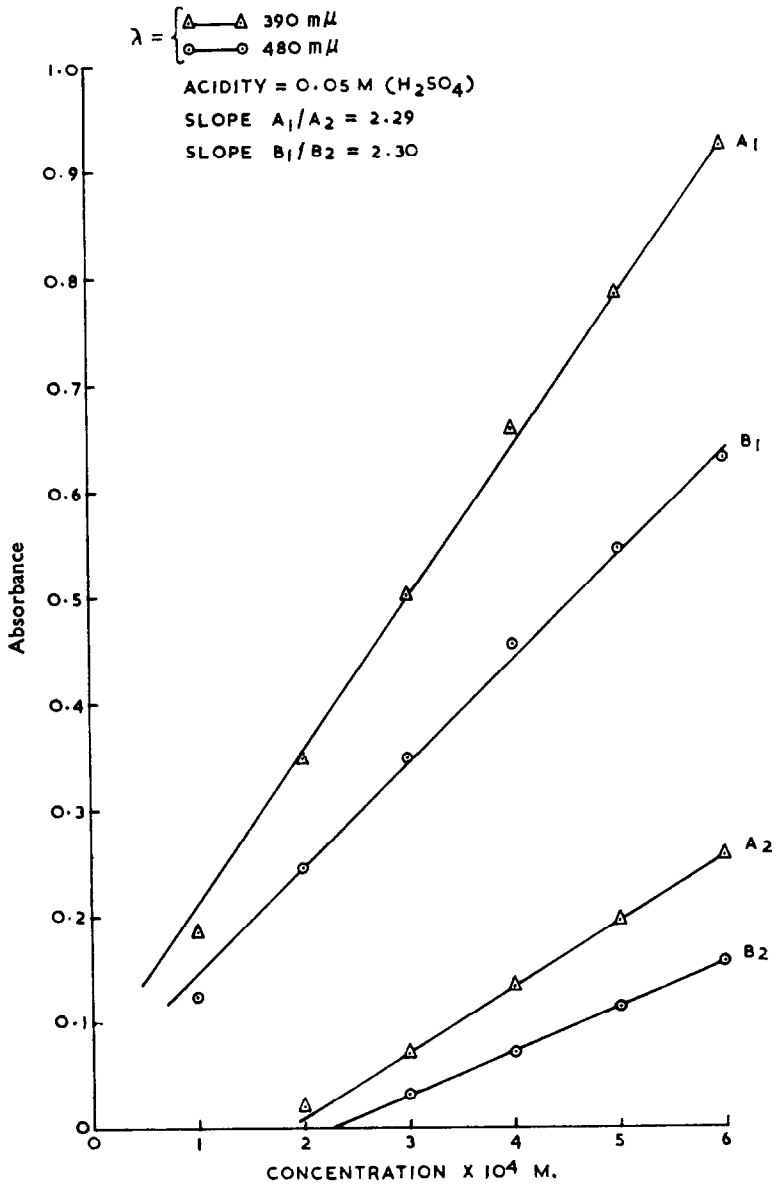

FIG. 6.—Nature of the vanadium(V)–oxine species extracted: slope-ratio method.

sufficiently high concentrations of oxine and n-butanol will be used, it may be concluded that the predominant species extracted has a 1:2:2 ratio of vanadium:oxine:n-butanol.

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Zusammenfassung—Die Extraktion und spektrophotometrische Bestimmung von Vanadium(V) mit Oxin wird bei höheren Aciditäten als den früher beschriebenen untersucht. Unter diesen Bedingungen wurde gefunden, daß n-Butanol und andere Alkohole einen synergistischen Einfluß auf die Extraktion von Vanadium in Benzol

ausüben. In Gegenwart von Alkohol wird nur ein 6-facher Ligandenüberschuß zur quantitativen Extraktion in einem einzigen Arbeitsgang benötigt, wenn die Acidität des wäßrigen Mediums 0,05 M bezüglich Schwefeloder Phosphorsäure ist. Störendes Eisen(III) wird bei der spektrophotometrischen Bestimmung von Vanadium durch Beigabe von Pyrophosphat unterdrückt. Das Beersche Gesetz gilt bis zu 14,0 μg Vanadium pro ml, die Empfindlichkeit ist 0,008 μg Vanadium pro cm^2 bei 390 nm. Die Zusammensetzung der extrahierten Spezies wurde als Vanadium: Oxin: n-Butanol = 1:2:2 gefunden.

Résumé—On étudie l'extraction et le dosage spectrophotométrique du vanadium(V) par l'oxine à des acidités plus fortes que celles décrites antérieurement. On a trouvé que, dans ces conditions, le n-butanol et d'autres alcools exercent un effect synergique sur l'extraction du vanadium en benzène. L'extraction quantitative en une seule opération ne nécessite, en présence d'alcool, qu'un excès de ligand égal à 6 fois la théorie, le milieu aqueux étant 0,05 *M* en acide sulfurique ou phosphorique. On supprime l'interférence du fer(III) dans le dosage spectrophotométrique du vanadium par l'addition de pyrophosphate. La loi de BEER est respectée jusqu'à 14,0 μg de vanadium/cm^3 et la sensibilité est de 0,008 μ de vanadium/cm^2 à 390 mμ. On a trouvé que la composition de l'espèce extraite est vanadium:oxine:n-butanol = 1:2:2.

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SIMULTANEOUS ESTIMATION OF COPPER, ZINC, CADMIUM AND MERCURY IN BIOLOGICAL MATERIAL BY NEUTRON ACTIVATION ANALYSIS

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Summary—Simultaneous determination of copper, zinc, cadmium and mercury with high sensitivity is possible by neutron activation analysis. After irradiation, the samples are digested and an initial separation of the four elements made by means of an ion-exchange resin. The elements in the separated fractions are then treated to give radiochemical purity, precipitated, and their activities measured. A purely instrumental technique for the analysis of zinc in samples of biological material is also described. The samples are irradiated for a week and after the activity has decayed for about three months it is measured on a gamma-spectrometer.

ALTHOUGH activation analysis methods are available separately for the determination of copper, zinc, cadmium and mercury, their determination together has not previously been described. This paper gives details for separating these elements and measuring their activity.

EXPERIMENTAL

Isotopes used

Of the isotopes produced by irradiation of copper, zinc, cadmium and mercury with thermal neutrons, some are not useful for analytical purposes, because of unsuitable half-lives or low activation cross-sections. The useful isotopes are 12·8-hr ^{64}Cu, 245-day ^{65}Zn, 57-min ^{69}Zn, 13·8-hr ^{69m}Zn, 53-hr ^{115}Cd, 43-day ^{115m}Cd, 2·4-hr ^{117}Cd, 65-hr ^{197}Hg, 24-hr ^{197m}Hg, and 47-day ^{203}Hg.

Some of these isotopes can be produced by reactions other than (n, γ), *e.g.*,

$$^{64}\text{Zn(n, p)}^{64}\text{Cu}$$
$$^{72}\text{Ge(n, }\alpha)^{69/69m}\text{Zn}$$
$$^{63}\text{Cu(n, }\gamma)^{64}\text{Cu} \xrightarrow{\beta^-} {}^{64}\text{Zn(n, }\gamma)^{65}\text{Zn}$$
$$^{115}\text{In(n, p)}^{115/115m}\text{Cd}$$
$$^{120}\text{Sn(n, }\alpha)^{117}\text{Cd}$$
$$\text{and } ^{203}\text{Tl(n, p)}^{203}\text{Hg}$$

There is no other apparent source of production of $^{197/197m}$Hg. The contributions from these reactions to the induced activity are insignificant unless the matrix contains large amounts of the parent elements, and can be ignored for biological materials.

Irradiation of samples

Irradiations are carried out with a thermal neutron flux of 10^{12} n cm^{-2} sec^{-1}. The duration of irradiation depends on which isotopes are used for the analysis. Different sensitivities and radiochemical contaminants arise from the use of various times of irradiation. With short irradiation the resultant activity, due to short-lived isotopes, decays rapidly and limits the time available for chemical separation. If a longer irradiation is used to produce the isotopes with long half-lives, more time is available for the chemical separation and many more samples can be handled; a further advantage is that direct access to a reactor near the laboratory is not essential.

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Three irradiation times are used: 1 hr for ^{69}Zn and ^{117}Cd: 1 day for ^{64}Cu, ^{69m}Zn and ^{115}Cd: 1 week for ^{64}Cu, ^{69m}Zn, ^{65}Zn, ^{115}Cd, ^{197}Hg, ^{197m}Hg and ^{203}Hg.

Preparation of samples

The materials dealt with are enamel sections from human teeth and tissue samples from post-mortem examinations. The amount of handling before irradiation is minimized to prevent contamination of the samples. The tissue samples are vacuum dried and stored in clean polyethylene envelopes. The enamel samples are obtained from teeth rinsed with distilled water and sectioned with a cutting disc. No contamination was found from this disc. For the 1-hr irradiation the samples are weighed into small clean polyethylene envelopes and packed for irradiation in $\frac{1}{4}$ in. diameter polyethylene containers along with zinc and cadmium standards. For the longer irradiations the samples are weighed and wrapped in aluminium foil and packed, with standards, in an aluminium irradiation can.

Preparation of standards

For the short irradiations standards are prepared from dilute aqueous solutions of high purity zinc and cadmium. A small volume of standard solution, containing 1–10 μg of the element, is evaporated on a piece of polyethylene sheet (previously cleaned with conc. nitric acid and distilled water) under an infrared lamp. For the 1-day irradiations standard solution is weighed into clean silica ampoules which are then carefully heat-sealed. After irradiation, the ampoules are opened and the contents washed into volumetric flasks and diluted appropriately. An aliquot of the diluted standard is used for comparison with the samples and is processed and counted in a similar manner. For 1-week irradiations, high purity solid standards are used in sub-milligram amounts. The amount of cadmium standard irradiated is kept as small as possible to avoid the effect of self-shielding, which could cause the specific activity induced in the standard to be lower than that induced in a very minute amount of the element in the samples.

Reagents

Where possible, analytical grade reagents are used. The anion-exchange resin is the strongly basic Amberlite IRA-400 (Cl form), used in 1-cm columns packed with a 7-cm length of resin.

The ammonium reineckate solution is not very stable and is prepared frequently.

Procedure

Place the irradiated samples and standard in 25-ml conical-bottomed flasks with 6-in. necks. Add 10 mg of copper, zinc, cadmium and mercury carriers to each flask. Digest the samples with 2 ml of a mixture of 16*M* nitric acid and 18*M* sulphuric acid (1 + 1). When dissolution is complete and all the nitric acid has been removed, dilute the solutions to 36 ml with 0·5*M* hydrochloric acid.

If mercury is not to be determined, decompose the samples as described or dissolve them, together with carrier, by heating with 3 ml of 16*M* nitric acid in 100-ml beakers, evaporate the solutions to dryness, add 1 ml of 11*M* hydrochloric acid and again take them to dryness. Dissolve the residues in 0·5*M* hydrochloric acid. Add 5 drops of 10% ammonium dihydrogen phosphate solution to the solution from the digestion stage. Precipitate zirconyl phosphate by adding 8 drops of 10% zirconyl chloride octahydrate solution and centrifuge it. Sulphuric and hydrochloric acids in concentrations less than 1*N* do not interfere significantly with the precipitation.

Transfer the 0·5*M* hydrochloric acid solution of the sample (from the digestion or the phosphate scavenge step) to a gravity-operated reservoir on top of the ion-exchange column, pass it through, and wash the column with 25 ml of 0·12*M* hydrochloric acid containing 10% w/v of sodium chloride. Elute the copper with 20 ml of 0·5*M* hydrochloric acid followed by 20 ml of 0·12*M* hydrochloric acid containing 10% w/v of sodium chloride. Elute the zinc (with some cadmium and mercury—see discussion below) at a flow-rate of 3 ml/min with 40 ml of 2*M* sodium hydroxide containing 2% w/v of sodium chloride. Elute the cadmium with a little mercury and the rest of the zinc by means of 50 ml of 1*M* nitric acid at a flow-rate of 3 ml/min. Strip the residual mercury from the column with 5% w/v ethylenediamine solution. Treat each of the four eluates as described below.

Copper. The hydrochloric acid eluate contains many other radioactive species besides copper, and Nixon and Smith's separation procedure[1] should be used. This entails precipitation of copper(I) thiocyanate in the presence of hold-back carriers, a scavenging step with hydrous iron(III) oxide, reprecipitation of copper(I) thiocyanate, and final precipitation of copper quinaldinate which is used as the weighing form for calculating chemical yield and also for the activity determination with an end-window Geiger counter.

Zinc. Make the eluate just acid by addition of concentrated hydrochloric acid, and add 0·5 ml of 10 % w/v iron(III) chloride solution as iron carrier. Add 3 ml of 5*M* sodium hydroxide, heat the

mixture on a water-bath, and centrifuge off the hydrous iron(III) oxide. Filter the supernatant liquid to ensure removal of all iron, neutralize it with glacial acetic acid to the phenolphthalein end-point and add another 1 ml of acetic acid. Heat the solution on a water-bath and precipitate the zinc by addition of 2% quinaldinic acid solution. Wash the precipitate once with water and once with acetone and slurry it onto a weighed aluminium planchet with acetone. Dry it under an infrared lamp at 100°, weigh the precipitate as $Zn(C_{10}H_6O_2N)_2H_2O$ and measure its activity with an end-window Geiger counter.

Cadmium. Make the cadmium effluent alkaline with 5*M* sodium hydroxide and centrifuge off the cadmium hydroxide. Dissolve the precipitate in 1 ml of concentrated hydrochloric acid, dilute the solution to 20 ml and add 5 ml of 5% thiourea solution and 8 ml of a solution of ammonium reineckate (saturated at 18°) containing 1% of urea. Wash the precipitated cadmium reineckate with 1% thiourea solution and absolute alcohol. Slurry it onto a weighed aluminium planchet with absolute alcohol, dry it under an infrared lamp, weigh it as $Cd[SC(NH_2)_2][Cr(NH_3)_2(SCN)_4]_2$ and count its activity with an end-window tube.

Mercury. Add 1 ml of 10% sodium iodide solution and 1 ml of 10% copper sulphate solution to the mercury eluate to precipitate the copper ethylenediamine—mercuric iodide complex,[2] wash the precipitate with water and isopropanol, transfer it to a stainless steel planchet, dry it at 90°, weigh it, and measure its activity with a sodium iodide (Tl) crystal and pulse-height analyser. For greatest sensitivity use the 78 keV photopeak of ^{197}Hg.

Count rates. All count-rates are corrected for background, decay and chemical recovery, and the metal content calculated in the usual way from the activity of sample and standard.

Instrumental method for zinc only

Some samples can be analysed for zinc by irradiating them (together with a standard) for a week at a flux of 10^{12}n cm^{-2} sec^{-1}, letting short-lived activities decay during 100 days, and then measuring the activity of the 1·12 MeV ^{65}Zn photopeak with a pulse-height analyser (3 in. sodium iodide (Tl) crystal, analyser window set to 1·00–1·25 MeV).

RESULTS AND DISCUSSION

Phosphate scavenge

Phosphorus is one of the major interfering contaminants in work with biological materials and any separation procedure must be tested to ensure that this interference is not present.

Experiments with ^{32}P tracer showed that no ^{32}P activity could be detected in the zinc quinaldinate precipitates, but it was found in the hydrochloric acid fraction first eluted from the ion-exchange column. However, decay measurements made on zinc quinaldinate precipitates separated from tissue samples irradiated for 24 hr indicate the presence of 14·2-day ^{32}P. It appears that because of the high phosphorus content of the samples being analysed, the amount of ^{32}P activity induced in the sample is many times greater than that used in the tracer experiments. A small fraction of this activity comes through the separation and consequently it is necessary to introduce the phosphate scavenge step before the ion-exchange procedure, if the irradiation time is 24 hr or longer. It is not necessary for samples of less than 10 mg irradiated for 1 hr.

Ion-exchange separation

The separation used is based on that reported by Kallmann, Steele and Chu[3] for the separation of zinc and cadmium. Tracer experiments show that zinc, cadmium and mercury are retained on the column, but cations and non-adsorbable anions are washed through.

Copper. As described by Kraus and Nelson,[4] bivalent copper is not retained on the resin from dilute solutions of hydrochloric acid. By use of ^{64}Cu tracer and zinc,

cadmium and copper carrier, it can be demonstrated that the copper is not retained on the resin but passes through in the hydrochloric acid fractions. The results are shown in Table I. No copper activity appears in the zinc or cadmium precipitates subsequently obtained.

Zinc. Zinc is eluted from the column by displacement of the chloro-complex of zinc and formation of the tetrahydroxozincate ion. Only amphoteric elements capable of forming alkali-soluble salts will be eluted with this fraction. Many other elements displaced from the resin by hydroxide form insoluble hydroxides or oxides. In the case of mercury and cadmium this can be seen by the formation of a yellow band of mercuric oxide or a grey band of cadmium hydroxide on the resin.

Some cadmium and mercury escape from the column. Kallman, Steele and Chu,[3] however, did not find cadmium in their zinc fractions when separating 1 g each of zinc and cadmium by this ion-exchange technique.

Tracer experiments with ^{115}Cd have been made to determine the behaviour of the cadmium in the ion-exchange procedure. This isotope has a daughter ^{115m}In with a half-life of 4·5 hr. The ^{115m}In activity is not adsorbed on the column, and this is in accordance with Kraus and Nelson's results for the adsorption of indium on Dowex 1 resins from hydrochloric acid solutions.[4] Counting was, therefore, delayed overnight to allow parent/daughter equilibration. The zinc fractions were acidified with concentrated hydrochloric acid on collection, to prevent possible mechanical loss of cadmium as cadmium hydroxide. The results are given in Table I. It can be seen that a total of about 5% of cadmium tracer is found in the zinc fraction. In addition, γ-spectrometry revealed the presence of cadmium activity in the final zinc quinaldinate precipitate if the iron hydroxide scavenge was omitted during analysis of tissues containing significant amounts of cadmium.

Similarly it is found that mercury escapes from the column with the zinc fraction. A typical experiment showed about 20% of the mercury tracer being eluted with the zinc (Table I). It is thought that these two effects are due to the retention mechanism for the cadmium and mercury.

Kallman, Steele and Chu[3] note that the mechanism of cadmium retention by the resin has not been established. They suggest that the presence of sodium chloride has some effect. The slight leakage of cadmium and mercury from the resin on elution with sodium hydroxide (Table I) leads to a suggestion of the manner in which these elements are retained.

This would probably also apply to other elements held on the resin and capable of forming insoluble oxides and hydroxides. When zinc is eluted with alkali in the presence of cadmium tracer and carrier, no activity is detected in the effluent fractions with a Geiger liquid-counter. When the fractions are made acid with hydrochloric acid, 4–5% of the cadmium tracer used is detected with the zinc fraction (Table I). It is probable that, in the alkaline medium, the cadmium is adsorbed on the walls of the collecting tube as cadmium hydroxide and is not transferred to the counting tube. When the fraction is made acid, the cadmium is dissolved and is transferred and counted. This problem does not arise in the case of zinc elution in the presence of mercury tracer and carrier as the eluted fractions are counted directly in a scintillation well crystal without being transferred from the collecting tube.

It is suggested that the retention of the cadmium and mercury bands on the resin is a mechanical retention of the insoluble hydroxide and oxide respectively. The

TABLE I.—ELUTION OF COPPER, ZINC, CADMIUM AND MERCURY

Eluent	Eluent volume, *ml*	Total tracer in fraction, % Copper	Zinc	Cadmium	Mercury
0·5*M* HCl	0–10	43·4	—	—	—
	10–20	53·9	—	—	—
0·12*M* HCl + 10% w/v NaCl	0–10	2·2	—	—	—
	10–20	—	—	—	—
2*M* NaOH + 2% w/v NaCl	0–10	—	29·7	1·8	7·6
	10–20	—	33·8	1·5	5·4
	20–30	—	12·5	1·0	5·4
	30–40	—	7·0	0·5	4·0
1*M* HNO_3	0–10	—	4·8	2·3	0·5
	10–20	—	5·7	45·5	—
	20–30	—	4·8	36·0	—
	30–40	—	2·8	9·0	1·1
	40–50	—	—	3·8	3·6
5% w/v $NH_2(CH_2)_2NH_2$	0–10	—	—	—	22·2
	10–20	—	—	—	18·3
	20–30	—	—	—	13·9
	30–40	—	—	—	8·8
	40–50	—	—	—	6·6
	50–60	—	—	—	1·5
Total tracer recovered		99·5	101·1	101·4	98·9

leakage from the column may be attributed to small particles of precipitate being separated from the main bulk of precipitate and washed down through the resin.

Cadmium. It was expected that mercury would contaminate the cadmium fraction but under the elution conditions the mercury is very difficult to remove from the resin and only about 5% of the tracer was found in the cadmium fraction (Table I).

Mercury. Kraus and Nelson[5] report that mercury is difficult to elute from an anion-exchange resin, on which it is adsorbed as its chloro-complex. Various solutions (Table II) were used in an attempt to remove the mercury from the resin after the cadmium elution.

The mercury carrier is precipitated on the column as mercury(II) oxide during zinc elution and is not eluted with 1*M* nitric acid although mercury(II) oxide dissolves readily in this concentration of acid and tracer experiments show that mercury is not retained on the resin when added to it in the nitrate form.

The reason for the ease of mercury elution with ethylenediamine is thought to be

TABLE II.—MERCURY ELUTION

Eluent	Mercury tracer in 50 ml of eluent, %
Nitric acid, 2*M*	19
Thiourea, 0·1*M*/hydrochloric acid, 0·01*M*	17
Hydrochloric acid, 9*M*	7
Sulphuric acid, 4·5*M*	8
EDTA (5% w/v), pH 4	11
EDTA (5% w/v), pH 7	14
EDTA (5% w/v), pH 9	19
EDTA (5% w/v), pH 11	18
Ethylenediamine (5% w/v), pH 2	27
Ethylenediamine (5% w/v), pH 7	49
Ethylenediamine (5% w/v), pH 12	71

the formation of the cationic species $Hg(OH)(en)_2^+$, $Hg(en)_2^{2+}$ or $Hg(en)_3^{2+}$, which are not held on an anion-exchange resin. As most complexing agents produce a negatively charged complex they would not elute mercury from this type of resin.

Final processing

Each of the solutions from the column requires to be further processed to give complete radiochemical purity and to prepare the element in a form suitable for making recovery estimations.

Copper. The radiochemical purity of the quinaldinate and the accuracy of the analysis are already established but these were checked again as follows. A series of copper quinaldinate precipitates prepared from activated biological tissue were checked exhaustively by γ-spectrometry and decay measurements, but all showed the activity present to be due exclusively to ^{64}Cu. A series of samples of a biological standard* were analysed and gave answers of 4·5, 4·5 and 4·9 ppm which compare well with the known value of 4·4 ppm and a range of 4·1–4·5 ppm obtained by the method of Nixon and Smith.[1]

Zinc. Of the elements adsorbable in the resin from dilute hydrochloric acid solutions, Cd, Zn, Ag, Pb, Hg(II), Pd(II), Pt(II) and Fe(III) are capable of forming quinaldinates. Of these, only zinc and lead form an alkali-soluble salt and hence are separated from the rest of these elements on elution of the zinc fraction. Under the activation conditions lead does not interfere but as noted before, there is a leakage of cadmium and mercury into the alkaline eluate. To eliminate this contamination, it is necessary to introduce a scavenging step before the final precipitation. The scheme used results in complete radiochemical purity, as can be shown by γ-spectrometry and decay studies.

A series of standard solutions was analysed to check the accuracy of the method and gave values which agreed with the calculated value within 5% for all the samples. Samples of the biological standard gave values of 34, 32 and 27 ppm which compare closely with the known value of 30 ppm.

Cadmium. Of the elements held on the resin with cadmium by formation of insoluble oxides or hydroxides, only Ag, Hg(II), Tl and Bi are precipitated with cadmium by Reinecke's salt. As shown in Table I, only about 5% of the mercury is eluted with the cadmium and it has not been found as a contaminant in the samples analysed in this work. It may well prove to be a contaminant in analysis of material relatively rich in mercury. If silver, mercury or thallium should prove to be a problem, they can be removed by a suitable silver chloride scavenge before the reineckate precipitation. Because of its poor activation characteristics, bismuth does not interfere in analysis of most biological materials.

A series of standard solutions was analysed to check the accuracy of the method and gave values which agreed with the calculated value within 5% in all the samples. Samples of the biological standard gave analysis values of 0·67, 0·63 and 0·60 ppm. No known figures are available for comparison. The precipitates were radiochemically pure.

Mercury. As shown in Table I, the chemical recovery of mercury may be as low as 60% because of losses during the separation procedure.

* Due to H. J. M. Bowen, Department of Chemistry, University of Reading, England.

The radiochemical purity of the final precipitates was determined by γ-spectrometry and only mercury activity was found to be present. A series of analyses of the biological standard gave values of 0·24, 0·21 and 0·24 ppm. Samples analysed by a method specific for mercury[2] gave values in the range 0·21–0·26 ppm.

Instrumental zinc analysis

Figure 1 shows the γ-spectra of a 40-mg sample of human tooth enamel, 9 and 100 days after the end of a 1-week irradiation. After 9 days the principal features of the spectrum are the ^{65}Zn photopeak at 1·12 MeV, the ^{24}Na photopeak at 1·37 MeV,

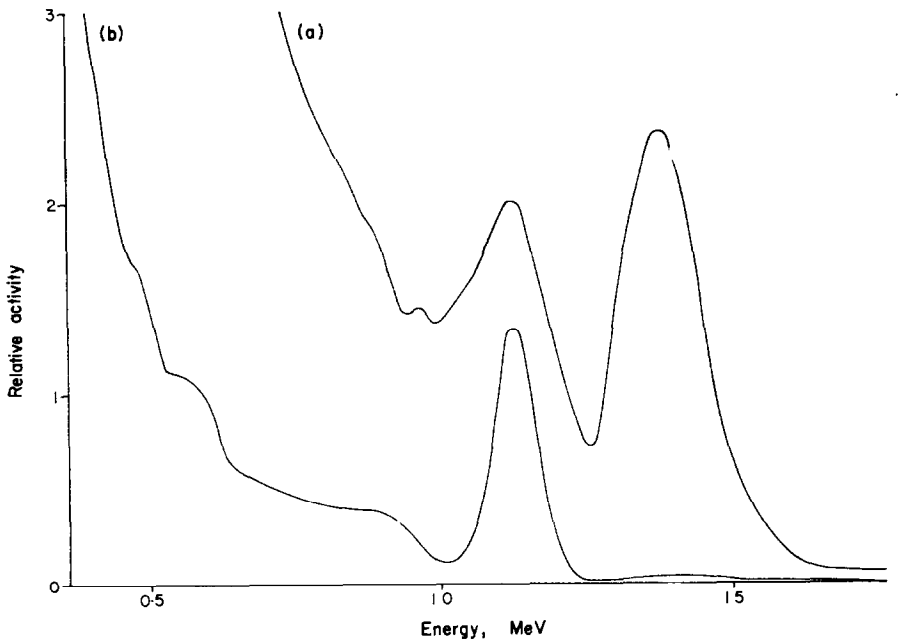

FIG. 1.—γ-Spectra of irradiated tooth enamel.
(a) 9 days after irradiation
(b) 100 days after irradiation

and the gross ^{32}P bremsstrahlung at the lower (<1 MeV) end of the spectrum. After 100 days the ^{24}Na photopeak ($t_{\frac{1}{2}}$ = 15·0 hr) has disappeared and the brehmsstrahlung effect from the ^{32}P ($t_{\frac{1}{2}}$ = 14·2 days) is greatly reduced. The spectrum above 0·5 MeV is essentially that of ^{65}Zn ($t_{\frac{1}{2}}$ = 245 days) and the 1·12 MeV photopeak is used for the zinc estimation.

As a check on the accuracy of the instrumental method a batch of samples (sections of the inner enamel cut from sound extracted human teeth) was analysed by the 1-hr irradiation method described and another batch was analysed by the instrumental method. A comparison of the results obtained is given in Table III. The weight of sample used is in the range 10–30 mg. The results show a good comparison of the two methods with reasonable agreement between the mean and median values. The spread of results is greater for the batch analysed by the instrumental method but this is not unexpected since more samples were analysed by this method.

TABLE III.—COMPARISON OF ZINC CONTENT OF INNER ENAMEL SECTIONS BY TWO METHODS OF ANALYSIS

	Zinc, *ppm*	
	Chemical method	Instrumental method
No. of samples analysed	16	60
Range	110–435	58–584
Mean value	255	236
Median value	224	209

Sensitivity

The sensitivities vary according to the experimental condition chosen. The major factors are the neutron flux and the irradiation time, which in turn depends on the isotope used. The limit of sensitivity is taken to be the amount of element needed to give a count-rate equal to the background count-rate of the detection instrument. The results are shown in Table IV.

TABLE IV.—TRACE ELEMENT SENSITIVITIES (μg)

Condition	Sensitivity at a neutron flux of 10^{12} n cm^{-2} sec^{-1}			
	Copper	Zinc	Cadmium	Mercury
1-hr irradiation	not used	0·01	0·1	not used
1-day irradiation	0·0005	0·1	0·01	not used
1-week irradiation	0·0005	0·1	0·001	0·0005
Instrumental analysis	—	1·0	—	—

As can be seen from the table, the choice of irradiation period affects the sensitivity attainable for both zinc and cadmium. For maximum sensitivity of analysis for zinc a short irradiation of $\frac{1}{2}$–2 hr is required. Maximum sensitivity for cadmium analysis is obtained by irradiating for a week, to give ^{115}Cd. The instrumental method of zinc analysis will often prove adequate for zinc determination in biological material. It has the advantage that a large number of samples may be analysed at a time since the long-lived ^{65}Zn eliminates the problem of completing the analysis in a short time interval. From our experience in zinc analysis of dry human tissue from various organs the amount of zinc in a 50-mg sample will be in the range 1–20 μg, which is readily detectable by this method.

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Zusammenfassung—Die gleichzeitige Bestimmung von Kupfer, Zink, Cadmium und Quecksilber mit hoher Empfindlichkeit ist möglich durch Neutronenaktivierungsanalyse. Nach Bestrahlung werden die Proben aufgeschlossen und mit Hilfe eines Ionenaustauschharzes die vier Elemente grob getrennt. Die Elemente in den abgetrennten Fraktionen werden dann radiochemisch gereinigt, gefällt und ihre Aktivitäten gemessen. Es wird auch ein rein instrumetalles Verfahren zur Bestimmung von Zink in Proben biologischen Materials beschrieben. Die Proben werden eine Woche lang bestrahlt. Nach dreimonatigem Abklingen der Aktivität wird sie an einem Gamma-Spektrometer gemessen.

Résumé—Le dosage simultané du cuivre, du zinc, du cadmium et du mercure avec une sensibilité élevée est possible par analyse par activation de neutrons. Après irradiation, les échantillons sont digérés et l'on effectue une séparation initiale des quatre éléments au moyen d'une résine échangeuse d'ions. On traite alors les éléments dans les fractions séparées pour avoir la pureté radiochimique, les précipite et mesure leurs activités. On décrit aussi une technique purement instrumentale pour l'analyse du zinc dans des échantillons de produits biologiques. On irradie les échantillons pendant une semaine et après affaiblissement de l'activité pendant environ trois mois, on la mesure avec un spectromètre gamma.

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VARIAMINE BLUE AS A GRAVIMETRIC REAGENT

DETERMINATION OF TUNGSTEN

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Summary—Tungsten can be precipitated by a solution of Variamine Blue at pH 5. The precipitate is ignited to constant weight at a temperature above 600° and weighed as tungsten trioxide. The method can be used for the determination of tungsten in alloy steels.

AMONG gravimetric methods for the determination of tungsten the one using precipitation in the form of tungstic acid ($WO_3 \cdot H_2O$) seems to be the simplest. Tungstic acid precipitated from acid solution, however, partly dissolves in water. Although the solubility can be reduced by dehydrating the precipitate at 120°, 1–3% of the precipitate dissolves on being washed with dilute acid. Tungstic acid dissolved this way cannot be precipitated again by repeated evaporation, and so low results are obtained by this method.[1]

Quantitative precipitation can be achieved, however, if the tungsten is precipitated in the form of the tungstate of an alkaloid or amine.[1–11] These precipitates are not of stoichiometric composition, and probably consist of tungstic acid binding variable amounts of organic reagent by adsorption. Precipitates formed with organic reagents have a favourable morphology and can be fairly easily ignited to tungsten trioxide.

Variamine Blue base* was found to be a suitable reagent for the quantitative precipitation of tungsten. Besides being an excellent redox indicator and colorimetric reagent,[12] it has been successfully used in qualitative analysis as a spot-test reagent.[13]

We found in our spot-test experiments that Variamine Blue produced an amorphous, greyish white precipitate with tungstate ions. This precipitate was soluble in dilute acids, so the detection could only be carried out in nearly neutral media. The detection limit was 1·8 μg, in a 1:544,000 dilution, and the sensitivity exponent p_D was 5·7. Molybdenum ions interfere by forming a precipitate of similar colour. The sensitivity of the reagent for molybdenum is one order of magnitude lower than that for tungstate ions, so that small amounts of molybdenum do not interfere.

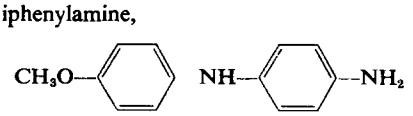
EXPERIMENTAL

Reagents

Sodium tungstate solution 0·02*M*, was prepared from analytical grade reagent (hydrated), and was standardized by the mercury(I) tungstate and benzidine tungstate gravimetric methods.

Variamine Blue solution was prepared by rubbing 1 g of reagent with 10 ml of 0·1*M* acetic acid, diluting to 100 ml with water and filtering through a G4 sintered glass crucible. This reagent can be used for 1–2 days, but it is advisable to prepare it freshly before use.

* 4-Amino-4′-methoxy-diphenylamine,



Optimum pH for precipitation

The pH of the nearly neutral stock solutions was varied between 0·3 and 6·0 by adding hydrochloric acid or acetic acid and the degree of precipitation was determined. The results are presented in Table I. Quantitative precipitation occurs at pH 5. At lower pH values tungsten is only partly precipitated, and the precipitate formed at pH 6 is very fine, and difficult to filter. The error of 2·5% is due to the fact that some of the precipitate passed through the filter. The precipitate formed at pH 5 is voluminous, settles quickly and is easy to filter.

TABLE I.—EFFECT OF VARIATION OF pH ON THE PRECIPITATION

True value, WO_3, *mg*	pH	Obtained, WO_3, *mg*	Deviation, %
92·4	0·3	82·9	−10·2
	1·0	83·1	−10·0
	3·0	90·3	−2·2
	4·0	91·6	−0·8
	5·0	92·4	±0·0
	6·0	86·0	−2·5

Solubility of the precipitate

Variamine Blue tungstate was precipitated from solutions at pH 4 and 5, filtered off on a G4 sintered glass crucible, washed with 0·01*M* acetic acid, and dried by sucking air through it for about 2 hr. The dry precipitate was agitated in 100 ml of 0·01*M* acetic acid at 26° for 4 hr and the solubility of the precipitate was determined by measuring the Variamine Blue concentration of the solution photometrically.

The calibration curve for the determination was prepared as follows: known amounts of 0·01*M* iron(III) chloride solution were added to solutions of Variamine Blue of known concentration, at a suitable pH. The optical densities of the solutions were measured with a Pulfrich photometer, an S57 filter being used. The amount of Variamine Blue due to the dissolution of the precipitate, and hence the solubility, was determined by measuring the optical density under the same conditions. The solubility in 0·01*M* acetic acid is $3·5 \times 10^{-5}$ mole/l if the precipitation is carried out at pH 5, and $8·5 \times 10^{-5}$ mole/l. for the precipitate produced at pH 4.

Temperature of precipitation

Table II shows the effect of temperature on the precipitation. The weights of the precipitates obtained at different temperatures are similar, but whereas the precipitate is formed instantaneously in a voluminous flaky form at room temperature and can be filtered off after 15 min settling, the one obtained at 50° is at first colloidal, and can only be filtered off after cooling with frequent stirring. It is difficult and tedious to transfer to the filter the traces of precipitate adhering to the wall of the beaker. These disadvantages are even more marked if the precipitation is carried out at the boiling point.

TABLE II.—EFFECT OF TEMPERATURE ON THE PRECIPITATION

True value, *mg*	WO_3 obtained by precipitation at		
	Room temperature *mg*	50° *mg*	100° *mg*
92·4	92·5	92·6	92·9

Heating of the precipitate

The Variamine Blue tungstate precipitate cannot be dried to constant weight. One might assume on the basis of the thermoanalytical curves of the precipitate (see Fig. 1) that a weighable precipitate, possibly of constant weight, can be obtained by drying between 110 and 200°. The weights of precipitates dried at the same temperature in this range were the same, but those of precipitates dried at different temperatures differed markedly, as is shown in Table III. The results obtained after drying at room temperature by passing air through the precipitate were also different.

Even if a precipitate of constant weight could be obtained by drying in a certain temperature range, it would not be reasonable to use a conversion factor calculated from the formula weight obtained by

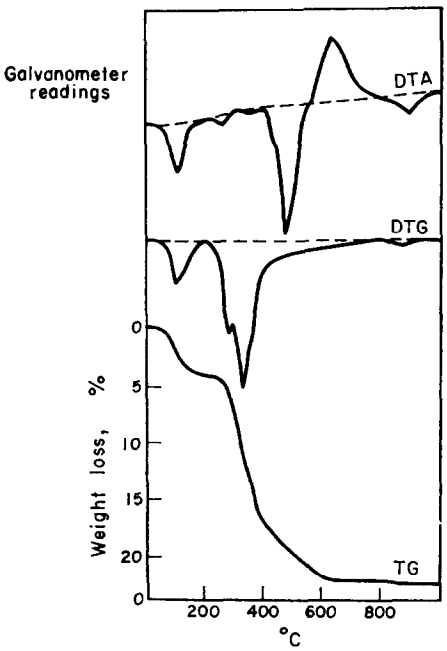


FIG. 1.—Thermogravimetric curves for the tungsten–Variamine Blue complex.

TABLE III.—DRYING OF THE PRECIPITATE

Temperature, °C	Weight of precipitate, *mg*			Mean, *mg*
Air suction (room temperature)	155·0	152·0	151·8	152·9
110	151·7	151·2	151·1	151·3
150	149·0	149·2	148·4	148·8
200	143·8	144·5	144·1	144·1

elementary analysis. Presumably, Variamine Blue tungstate, like other amine tungstates, is an adsorption compound of variable composition and loose structure. This is also shown by the infrared spectroscopic data. The infrared spectrum of the precipitate was nearly the same as that of Variamine Blue itself, which suggests that no molecular bonding exists between the constituents.

Collecting the precipitate on filter paper and igniting it at temperatures above 600° gives reproducible and accurate results. Table IV, presenting results obtained for various amounts of precipitate, shows the reproducibility of the method.

The accuracy and standard deviation of the measurements were determined on the basis of six parallel measurements. In the case of precipitate weights of 92·4 mg the deviation from the mean was found to be +0·2%, while the standard deviation was 0·16 mg, i.e. the coefficient of variation was 0·2%.

Among foreign ions, halides, sulphates, nitrates, thiocyanates and silicates of alkali metals, and copper, arsenic(III), cobalt(II), nickel, aluminium, zinc, manganese and ammonium ions do not interfere with the determination.

Heavy metal ions, such as silver, lead and mercury(I), and also calcium and barium ions, produce a precipitate with tungsten and interfere with the determination.

TABLE IV.—PRECIPITATION OF VARIOUS AMOUNTS OF TUNGSTEN

WO_3				
True value, *mg*	Found, *mg*	Mean, *mg*	Deviation, *mg*	*%*
45·8	45·2 45·7 45·2	45·4	−0·4	−0·9
92·4	92·7 92·3 92·3	92·4	0·0	0·0
231·0	230·9 231·6 231·2	231·3	+0·3	+0·1

Oxidizing agents also interfere, because no precipitate is formed in their presence; such are iron(III), chromium(VI) and cerium(IV) ions. Molybdate ions give a precipitate with Variamine Blue. The effect of iron(III) can be eliminated by reduction with ascorbic acid or masking with EDTA, but molybdenum must be separated before precipitation. Phosphate and chromium(III) also interfere.

Procedure

Add to the nearly neutral or neutralized solution containing 40–200 mg of tungsten, 10 ml of 0·1*M* acetic acid and dilute to about 100 ml with water. After adding 20–30 ml of Variamine Blue reagent solution, stir the quickly settling, flaky precipitate several times with a glass rod, then filter it off on a medium porosity filter paper after about 15 min standing. Wash with a solution consisting of 100 ml of 0·1*M* acetic acid and 10 ml of Variamine Blue reagent solution mixed and diluted to 300 ml with water. After washing, ignite the precipitate in a porcelain or platinum crucible to constant weight at 600–700°, and weigh the tungsten trioxide obtained.

PRACTICAL APPLICATION OF THE METHOD

The procedure has been utilized for the determination of tungsten in steel. The acid solution of the steel sample was passed through an ion-exchange column and tungsten was eluted and then precipitated with Variamine Blue.

Wilkins's method was used for the separation by ion-exchange,[14,15] as it was worked out for the determination of components of alloy steels. Strongly basic Dowex I resin, in a polythene tube, was converted into the chloride form with hydrochloric acid, and then washed with 2·5% hydrofluoric acid solution.

The sample was dissolved in a mixture of hydrofluoric, hydrochloric and nitric acids, the solution was evaporated to dryness, and the solid residue was dissolved in hydrofluoric acid, diluted with water and washed into the column with 2·5% hydrofluoric acid solution. Iron, cobalt, nickel, chromium, manganese, aluminium and copper were contained in the eluate. Titanium, tungsten, molybdenum and tantalum were bound on the column. First titanium was eluted, with 8*M* hydrochloric acid, then tungsten, with a solution consisting of 10 ml of 40% hydrofluoric acid and 60 ml of conc. hydrochloric acid mixed and diluted to 100 ml with water.

Sulphuric acid was added, and the solution was evaporated to fumes of sulphur trioxide, to remove fluoride. The solution was then diluted with water, neutralized with ammonia solution, and the pH adjusted by addition of an acetic acid—acetate buffer solution of pH 5. The precipitation was effected by the method described above. The precipitate was then filtered off, washed, and ignited and weighed as tungsten trioxide. The tungsten content of a steel sample containing 17·4% of tungsten was found to be 17·6 % by our method.

Our method has the advantage over others using other organic reagents, that the precipitate has favourable morphologic properties and can be filtered off shortly

after the precipitation. The Variamine Blue precipitate can be fairly easily converted into pure yellow tungsten trioxide, by igniting at above 600°.

Zusammenfassung—Wolfram kann durch eine Lösung von Variaminblau bei pH 5 gefällt werden. Der Niederschlag wird bei einer Temperatur oberhalb 600° bis zur Gewichtskonstanz geglüht und als Wolframtrioxyd gewogen. Die Methode kann zur Bestimmung von Wolfram in legierten Stählen verwendet werden.

Résumé—On peur précipiter le tungstène par une solution de Bleu Variamine à pH 5. Le précipité est calciné à poids constant à une température supérieure à 600° et pesé à l'état de trioxyde de tungstène. On peut utiliser la méthode pour le dosage du tungstène dans des alliages d'acier.

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SHORT COMMUNICATIONS

Radiometric determination of submicrogram amounts of mercury

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EXCHANGE reactions between a metal to be determined and a complex of another metal with lower stability or extraction constant are often used in analytical chemistry. With the use of radioisotopes the sensitivity of determinations of this type can be greatly increased.

In the present paper a radiometric method for the determination of mercury by exchange with silver–110m dithizonate is described. From the extraction constants of the metal dithizonates[1,2] it follows that silver is completely exchanged by mercury according to the reaction:

$$2\ {}^{110m}Ag(HDz)_{(org)} + Hg^{2+} = Hg(HDz)_{2(org)} + 2\ {}^{110m}Ag^{+}.$$

Preliminary experiments showed that equilibrium for this reaction is reached within 1 min. The amount of mercury present can be found from the decrease in the radioactivity of the silver–110m dithizonate in the organic phase or from the increase in the radioactivity of the silver–110m cations in the aqueous phase.

General procedure

To 8 ml of the test solution (pH 1-2) containing 0·01–0·10μg of mercury, add 1 ml of 5% urea solution and 1 ml of 10M acetic acid (previously purified by dithizone extraction). Transfer the solution into a separating funnel, and add 1·00 ml of $10^{-6}M$ silver–110m dithizonate in carbon tetrachloride.* Shake the funnel for 2–3 min, transfer 0·50 ml of the organic phase into an aluminium planchette, evaporate to dryness and measure the activity with a Geiger-Müller counter. A typical calibration curve is linear and has a slope of -1400 cpm silver activity/10^{-8} g of mercury/ml.

For determination of mercury in amounts ten times as great, use $10^{-5}M$ silver–110m dithizonate. The specific activity of silver–110m available permits the determination of mercury down to 5×10^{-10} g/ml with sufficient precision. The method is rather selective; only palladium, gold, silver and large amounts of copper and bismuth interfere, and these must be removed.

Procedure in the presence of palladium, copper and bismuth

To 8 ml of the test solution in 1M sulphuric acid, containing 0·1–1·0μg of mercury and 20 times as much palladium or 100 times as much copper and bismuth, add 1 ml of 0·01M 8-hydroxyquinoline solution in 10M acetic acid. Extract palladium (and partially copper and bismuth) as the 8-hydroxyquinolinate several 5 ml portions of chloroform. To the aqueous phase, still containing all the mercury, add 1·00 ml of $10^{-5}M$ silver–110m dithizonate in carbon tetrachloride, and test the solution as previously described. The amount of mercury is found from the calibration curve.

Procedure in the presence of silver

To 8 ml of the test solution (pH 1–3) containing 10–100 times as much silver as mercury, add 1 ml of 5% urea solution, 1 ml of 10M acetic acid and 1·3 g of solid sodium chloride (the total concentration of chloride ions is then about 12·5%). Extract the mercury quantitatively with an excess of dithizone solution in carbon tetrachloride (for 0·1–1·0μg of mercury use 2·00 ml of $10^{-5}M$ dithizone solution), leaving the silver completely in the aqueous phase. Transfer 1·00 ml of the organic extract into another separating funnel, and shake it for 2 min with an excess of silver–110m nitrate solution containing 0·5% of urea and 1M acetic acid. Transfer 0·50 ml of the organic extract to a planchette, evaporate it to dryness and measure the activity with a Geiger-Müller counter. The amount of mercury in the test sample is determined from a calibration curve prepared under the same conditions as before.

* This solution is prepared by shaking $10^{-6}M$ dithizone solution in carbon tetrachloride with an excess of silver–110m nitrate solution containing 0·5% of urea and 1M acetic acid. Thus prepared, and kept in the dark, the solution is stable for at least two days.

TABLE I.—DETERMINATION OF MERCURY IN THE PRESENCE OF FOREIGN METALS

Mercury taken, μg	Foreign metals present, μg	Mercury found, μg	Error, %
0·100	—	0·103	3
0·100	10 Cu	0·102	2
0·100	10 Bi	0·102	2
0·100	2 Pd	0·100	0
0·200	—	0·198	−1
0·200	20 Cu	0·205	2·5
0·200	20 Bi	0·213	6
0·200	4 Pd	0·208	4
0·300	—	0·304	1
0·300	30 Cu	0·302	1
0·300	30 Bi	0·299	0
0·300	6 Pd	0·303	1
0·400	—	0·405	1
0·400	40 Cu	0·405	1
0·400	40 Bi	0·394	1·5
0·400	8 Pd	0·396	−1
0·500	—	0·493	−1
0·500	50 Cu	0·489	−2
0·500	50 Bi	0·504	1
0·500	10 Pd	0·506	1

The procedure described is very simple and rapid. It permits the determination of as little as 5×10^{-10} g of mercury/ml with high selectivity (only gold interferes). Methods of this type are especially suitable when a radioisotope of high specific activity of the element to be determined is not available. Some typical results are shown in Table I.

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Summary—A radiometric method for the determination of submicrogram amounts of mercury (down to 5×10^{-10} g/ml) is described. The method is based on the exchange reaction between mercury and silver–110m dithizonate. Only palladium, gold, silver, and large amounts of copper and bismuth interfere in the determination, and must be removed.

Zusammenfassung—Es wird eine radiometrische Methode zur Bestimmung von Submikrogrammengen Quecksilber (bis herunter zu $5 . 10^{-10}$ g/ml) beschrieben. Die Methode beruht auf der Austauschreaktion zwischen Quecksilber und Silber–110m-Dithizonat. Nur Palladium, Gold, Silber und große Mengen Kupfer und Wismut stören bei der Bestimmung und müssen entfernt werden.

Résumé—On décrit une méthode radiométrique de dosage de quantités de mercure inférieures au microgramme (jusqu'à 5×10^{-10} g/ml). La méthode est basée sur la réaction d'échange entre le mercure et le dithizonate d'argent–110m. Seuls le palladium, l'or, l'argent, et de fortes quantités de cuivre et de bismuth gênent le dosage et doivent être éliminées.

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Extractive photometric determination of thorium with arsenazo DAL

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ARSENAZO III, (3,6-bis(2'-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulphonic acid) is a well known photometric reagent, employed for determination of actinides, lanthanides, zirconium, hafnium, yttrium and scandium.[1] The methods with arsenazo III are usually used for homogeneous aqueous/non-aqueous solutions, because of the hydrophilic sulphonic groups in the reagent molecule. An extractive modification is based on the blocking of the hydrophilic character of the sulphonic acid groups by salt formation with *sym*-diphenylguanidine.[2-4] A considerable disadvantage of this procedure is the contamination of the aqueous phase by the excess of *sym*-diphenylguanidine, which makes it difficult to use without a preliminary removal of the *sym*-diphenylguanidine. This disadvantage can be eliminated by blocking the hydrophilic character of the sulphonic groups by sulphonamide formation. Arsenazo DAL, *i.e.*, the dianilide of 3,6-bis(2'-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulphonic acid forms extractable metal chelates with the same elements as arsenazo III. The reagent can be used for the determination of thorium, DCTA being used as masking agent.

EXPERIMENTAL

Preparation of the reagent solution

Dissolve 93 mg of arsenazo DAL[5] in about 250 ml of 0·1*M* sodium hydroxide. Add 1000 ml of n-butanol and about 250 ml of 0·5*M* hydrochloric acid. Shake for 1–2 min and then separate the

TABLE I

Th taken, μg	Metals added, μmole		Th found, μg	Th taken, μg	Metals added, μmole		Th found, μg
5·0	Cu(II)	10	4·8	5·0	Fe(III)	10	5·1
10·0		20	10·1	10·0		20	10·0
15·0		30	14·8	15·0		30	14·9
10·0		40	9·9	10·0		40	10·2
5·0		50	5·1	5·0		50	5·1
5·0	Cd	10	4·9	5·0	Co(II)	10	4·8
15·0		30	15·2	15·0		30	15·0
5·0		50	5·0	5·0		50	5·2
5·0	Y	10	5·1	5·0	Ni	10	5·1
15·0		30	14·9	15·0		30	14·8
5·0		50	5·2	5·0		50	5·1
5·0	La	10	5·0	5·0	Pb(II)	10	5·2
15·0		30	15·1	15·0		30	15·3
5·0		50	5·2	5·0		50	5·1
5·0	Zr	10	4·9	5·0	Bi	10	5·1
10·0		20	10·2	10·0		20	9·8
15·0		30	14·9	15·0		30	15·0
10·0		40	9·9	10·0		40	9·8
5·0		50	5·2	5·0		50	5·1
5·0	Hf	10	5·0	5·0	Mn(II)	10	5·1
15·0		30	14·8	15·0		30	14·8
5·0		50	5·2	5·0		50	4·9
5·0	Zn*	1000	4·8	5·0	U(VI)*	1000	5·1
10·0		2000	9·9	10·0		2000	10·1
15·0		3000	14·9	15·0		3000	15·0
5·0		4000	4·9	5·0		4000	5·2
5·0	V(V)*	1000	4·9	5·0	Mo(VI)*	1000	5·1
10·0		2000	10·1	10·0		2000	10·2
15·0		3000	14·8	15·0		3000	15·0
5·0		4000	5·1	5·0		4000	5·1

* Extraction with tri-iso-octylamine was used.

layers. Wash the butanol phase 3–4 times with 250 ml of water until the pH of the aqueous phase is 5–6. The reagent is used directly after washing.

A 0·01*M* solution of the diammonium salt of DCTA (1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetra-acetic acid) is prepared by dissolving 3·46 g of DCTA in 200 ml of 0·1*M* ammonia and diluting to 1 l. with water.

Procedure

Dissolve a sample containing 1–25 μg of thorium in hydrochloric acid of such concentration as to yield 1·2*M* acid after dilution to 10 ml. Add 5 ml of 0·01*M* diammonium-DCTA and dilute with water to 10 ml. Add 10·0 ml of the reagent solution and shake vigorously for 3–5 min. After clarification of the butanol phase, place an appropriate volume of it in a 1-cm cell and measure the absorbance at 654 mμ against a reagent blank.

RESULTS AND DISCUSSION

Typical results for several samples are summarized in Table I. Amounts of 30–50 μmole of other metal ions such as copper(II), beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, mercury(II), scandium, yttrium, lanthanides, aluminium, gallium, indium, thallium(III), titanium(IV), zirconium, hafnium, germanium, tin(IV), lead(II), vanadium(V), niobium(V), bismuth, chromium(III), molybdenum(VI), tungsten(VI), uranium(VI), manganese(II), iron(III), cobalt(II), nickel, ruthenium(IV) and palladium(II) do not interfere. In addition, 1-mmole amounts of alkali metal cations and common anions, such as chloride, bromide, nitrate, sulphate, perchlorate, acetate, EDTA, citrate, and tartrate, do not interfere.

Larger amounts, 1–4 mmole of uranium(VI), vanadium(V), niobium(V), cobalt(II), copper(II), iron(III), chromium(VI), molybdenum(VI), zinc and cadmium, can be removed by extraction from 7*M* hydrochloric acid with three 20-ml portions of 20% w/v solution of tri-iso-octylamine in xylene. The excess of acid is evaporated before the determination of thorium.

TABLE II

Metal ion	Cu(II)	Ca	Ba	La	Zr	Th	U(VI)
Optimum pH of extraction	4·3	1·2	5·9	5·9	1·2	†	5·9
Molar ratio metal/ligand in the extracted complex	—	—	—	1:1	1:1	1:2	1:1
Net molar absorptivity of the complex*	25·1 $\times 10^3$	1·2 $\times 10^3$	3·4 $\times 10^3$	20·5 $\times 10^3$	12·0 $\times 10^3$	36·0 $10^3 \times$	26·0 $\times 10^3$
Optimum wavelength, mμ	632	675	675	673	616	654	658

* In cm^2 $mmole^{-1}$, calculated for organic phase only.
† 1·2*M* Hydrochloric acid in the aqueous phase.

The optimum acidity conditions for extraction of some metal ions with arsenazo DAL, the molar ratio metal/ligand, and the molar absorptivities of the complexes formed are given in Table II. The ratio metal/ligand has been determined by the molar ratio method. The thorium and zirconium complexes are precipitated if the molar ratio metal/reagent is higher than 1:1.

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Summary—Arsenazo DAL, the dianilide of 3,6-bis(2′-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulphonic acid, is proposed as an extractive photometric reagent for the highly selective determination of trace amounts of thorium.

Zussammenfassung—Arsenazo DAL, d.h. Dianilid der 3,6-Bis(2'-arsonophenylazo)-4,5-dioxy-2,7-naphthalindisulfonsäure, wird als extraktionsphotometrisches Reagens zur hochselektiven Bestimmung von Spurenmengen des Thoriums vorgeschlagen.

Résumé—On propose le arsenazo DAL, c'est-á-dire le dianilide de l'acide 3,6-bis(2'-arsonophénylazo)-4,5-dihydroxy-2,7-naphthalenedisulphonique, comme réactif photometrique par extraction pour le dosage de traces de thorium.

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ANNOTATION

The stability constants of TAR and PAR complexes

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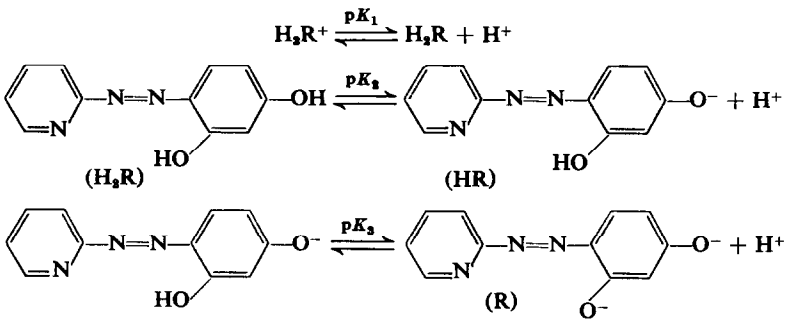
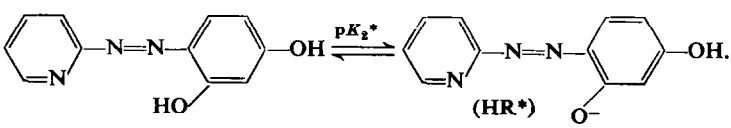
THE reagent 4-(2-pyridylazo)resorcinol (PAR) dissociates according to the reaction scheme



and 4-(2-thiazolylazo)resorcinol (TAR) behaves similarly. When these reagents form metal complexes, however, the complexes are formed at a pH too low for dissociation of a proton from the hydroxy group *para* to the azo group, and a proton is displaced from the *o*-hydroxy group although this proton would normally be the last to dissociate. The proton of the *o*-hydroxy group in the free reagent is involved in internal hydrogen bonding with the azo group, and so is normally less labile than the *p*-hydroxy group proton. In order to derive a stability constant for the complex formed between a metal ion M and the reagent, it is necessary to measure the equilibrium constant for the reaction

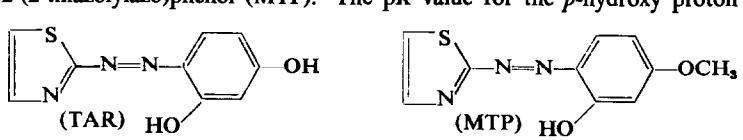
$$M + H_2R \rightleftharpoons MRH^* + H$$

where MRH* represents the complex, and then to ascribe a dissociation constant pK_2^* to the proton of the *o*-hydroxy group for the hypothetical situation in which it is assumed to be dissociated before the proton of the *p*-hydroxy group:



Most workers[1-3] have taken the view that this dissociation constant should be taken as equal to the dissociation constant that this group has *after* dissociation of the *p*-hydroxy proton (*i.e.*, $pK_2^* = pK_3$) but others[4] have taken the view that the dissociation constants should be interchanged (*i.e.*, $pK_2^* = pK_2$). Neither view is "correct", because it is impossible to assess the magnitude of the effect of the hydrogen bonding, but on balance it seems preferable to take pK_2^* as equal to pK_2, for the following reasons: (*a*) the contribution of internal hydrogen bonding to increase in p*K* for the *o*-hydroxy proton would be expected to be small compared with the inductive effect of the dissociated *p*-hydroxy group, and (*b*) there seems to be no reason why, in the absence of the hydrogen bonding effect, the *o*-hydroxy group should not be as least as acidic as the *p*-hydroxy group.

Support for this view comes from consideration of the dissociation constants for TAR and for 5-methoxy-2-(2-thiazolylazo)phenol (MTP). The p*K* value for the *p*-hydroxy proton in TAR in



aqueous medium is 6·2, and for the *o*-hydroxy proton in MTP is 6·7.[5] If we assume that the inductive effect of the methoxy group is very nearly that of the hydroxyl group, then the difference in the pK's would give a value of about 0·7 kcal/mole for the internal hydrogen bonding. This value may be compared with the 2 kcal/mole found by Franc[6] for the internal hydrogen bond in 2-methylresorcinol. It should be pointed out here that a change of 1 kcal/mole in ΔG is equivalent to a change of about 0·7 in pK.

It may be argued that the acidity of the *p*-hydroxy group is enhanced by resonance in the conjugated system (leading to a quinonoid structure for the resorcinol moiety), but this immediately leads to the difficulty that this resonance is not possible for the methoxy derivative, yet the acidity of the *o*-hydroxy group of MTP is not much less than that of the *p*-hydroxy group of TAR. This substantiates the view that the decisive factor is the hydrogen bonding and that the strength of the hydrogen bond is probably not more than 2 kcal/mole and may well be less than 1 kcal/mole.

It would be instructive to prepare the compounds 5-methoxy-2-(2-pyridylazo)phenol and 2-(2-thiazolylazo)resorcinol, and to measure the dissociation constants for the hydroxy group protons. The results should give a better estimate of pK_2* for PAR and TAR. Until this has been done, the best value to use for pK_2* would be pK_2 for the corresponding 5-methoxy compound.

At present, with two sets of conventions, it is necessary to perform a calculation to compare different sets of results. It will, of course, always be the case that the stability constants obtained will be artificial, but the difference between the "true" and reported values could be minimized by using the most realistic value for the estimate of pK_2*. As things stand, values for the stability constants obtained by Stanley and Cheney's method of calculation will be greater than those obtained by Sommer and Hniličková's method, by a factor of K_2/K_3 for the reagent concerned.

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Summary—A discussion is given of the problem of ascribing dissociation constants in the hypothetical situation in which the protons of the hydroxy groups of TAR and PAR dissociate in the reverse of the normal order, and it is suggested that the *o*-hydroxy group should be regarded as intrinsically as acidic as the *p*-hydroxy group, and that the change in pK due to the internal hydrogen bonding is probably less than one unit.

Zusammenfassung—Das Problem der Zuordnung von Dissoziationskonstanten wird in der hypothetischen Situation diskutiert, in der die Hydroxylprotonen von PAR und TAR in umgekehrter Reihenfolge wie üblich dissoziieren. Es wird vorgeschlagen, die *o*-Hydroxylgruppe als im wesentlichen ebenso sauer wie die *p*-Hydroxylgruppe zu betrachten; die pK-Änderung auf Grund der inneren Wasserstoffbrücke kann möglicherweise kleiner als eine Einheit sein.

Résumé—On présente une discussion sur le problème de l'attribution de constantes de dissociation dans la situation hypothétique où les protons des groupements hydroxy des TAR et PAR se dissocient de façon inverse de l'ordre normal, et l'on suggère que le groupement *o*-hydroxy devrait être considéré comme intrinsèquement aussi acide que le groupement *p*-hydroxy, et que le changement de pK dû à la liaison hydrogène interne est probablement inférieur à une unité.

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SEPARATION OF TIN FROM OTHER ELEMENTS BY PARTITION CHROMATOGRAPHY*

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Summary—Tin(IV) is separated quantitatively from many other metal ions by reversed-phase chromatography on a column of solid support impregnated with an organic liquid. When aqueous 8*M* hydrochloric acid is used as the eluent, tin(IV) is retained on a column impregnated with methyl isobutyl ketone and is separated quantitatively from bismuth(III), cadmium(II), copper(II), lead(II), mercury(II) and zinc(II). For the separation of tin(IV) and molybdenum(VI) the aqueous eluting phase is 1*M* hydrochloric acid–3*M* sulphuric acid. A column impregnated with isopropyl ether quantitatively retains antimony(V) from 8*M* hydrochloric acid and permits tin(IV) to be eluted rapidly.

METHODS for the analytical separation of tin from other elements include precipitation, volatilization and distillation, ion-exchange, electro-deposition and solvent extraction. These methods have their virtues but also have certain shortcomings and limitations. The object of the present research is to examine some solvent extraction methods with the goal of adapting these to useful separations of tin from other metal ions by column partition chromatography.

It has been known for some time that tin(IV) is partially extracted from aqueous hydrochloric acid solutions into ethyl ether,[1] but little use has been made of this information because the extraction is not quantitative. Orlandini *et al.*[2] studied the extraction of tin and other metal ions from aqueous hydrochloric acid into 2-ethylhexanol. Goto, Kakita and Furukawa[3] gave data for extraction of various metal ions from aqueous hydrochloric acid into methyl isobutyl ketone (MIBK), and Maeck *et al.*[4] studied the effect of quaternary ammonium salts on extractions into MIBK.

In the present research, data are given for the MIBK batch extraction of tin(IV) from hydrochloric, hydrochloric–hydrofluoric and hydrochloric–sulphuric acid solutions. Based on these results methods are developed for quantitative separation of tin(IV) from other metal ions by reversed-phase partition chromatography. These methods separate tin(IV) from most other metal ions that frequently occur with tin and are reasonably quick and easy to carry out.

EXPERIMENTAL

Apparatus and materials

The columns used were prepared by the following method. A perforated Teflon disc (Fischer and Porter Co.) was supported on the end of a Pyrex tube by means of a Teflon straight union reducer tube fitting (Beckman Instruments, Inc.). A straight bore stop-cock with a Teflon plug was connected to the lower end of the Teflon tube fitting.

* Work was performed at the Ames Laboratory of the U.S Atomic Energy Commission. Contribution No. 1994.

Columns of any length could be prepared easily by cutting off the glass tubing at the proper length. The flow-rate was regulated by means of compressed air. A one-hole rubber stopper with a short piece of glass tubing through it was inserted at the top of the column. One end of the glass tubing was then connected to a compressed-air line. In most cases only a small amount of air pressure was required to maintain a sufficient flow-rate.

The solvents methyl isobutyl ketone (MIBK) and isopropyl ether (IPE) were Eastman White Label and were distilled before use.

Teflon-6, a hard polyfluoroethylene, was obtained as a pre-sieved 160–170 mesh or 60–70 mesh powder from Analytical Engineering Laboratories, Hamden, Connecticut. Before use the powder was washed with 6*M* hydrochloric acid and acetone and then air-dried.

Chromosorb W was obtained as the 80–100 mesh fraction from Johns-Manville Corp. It was washed with 6*M* hydrochloric acid and acetone. It was air-dried and then refluxed with dichlorodimethylsilane in carbon tetrachloride and methanol to obtain a product that was more useful for reversed-phase chromatography.

All aqueous eluents were prepared in the proper acid concentration and were equilibrated with equal volumes of the organic phase by shaking for at least 1 min in separatory funnels.

In general, metal ion stock solutions were prepared in aqueous hydrochloric acid and aliquots were taken for standardization. Tin(IV) fluoride was prepared by dissolving tin metal in hydrofluoric and nitric acids. Test portions of fluoride solutions were taken by weight rather than by volume.

Column preparation

Column supports were first slurried in a portion of equilibrated organic solvent and allowed to remain in contact with the organic solvent for several hours to assure complete saturation. The slurry was then transferred to the chromatographic column, and a porous Teflon disc was placed on top of it to prevent the top of the support from being disturbed during addition of sample or eluent. A sufficient amount of equilibrated acid was passed through the column to displace any interstitial organic solvent on the column. An amount of equilibrated acid equivalent to the interstitial column volume, V_m, was sufficient for this purpose. This step was important because any excess of organic phase could bleed off the column during elution and carry with it a portion of the solute intended to remain on the column. The organic phase was run down to the level of the top of the column before the equilibrated acid was added.

The equilibrated acid was run down to the level of the top of the column and the sample was then added to the column by pipette. The sample was carefully sorbed onto the column by lowering the liquid level to the top of the support and then washing the sides of the column with three consecutive portions of equilibrated aqueous eluent, each time running off liquid to lower the level to the top of the column before the next portion was added. The column was then treated with the appropriate equilibrated aqueous eluent, and the solute extracted into the stationary phase was then washed off the column with equilibrated organic eluent of the same type as that used as the stationary phase. By this procedure the column was reconditioned with the organic phase at the same time as the elution was taking place, thereby replacing any of the organic stationary phase that might have been lost during the preceding elution. After repetition of the step of forcing enough equilibrated acid through the column to remove the interstitial organic phase, the column was ready to be used again and was in exactly the same condition as it was originally.

Methods of analysis

Tin(IV) was determined by the following procedure. The solution was acidified with hydrochloric acid to a pH of 1 or less to prevent the tin(IV) from hydrolysing. Then 2 g of sodium chloride and a moderate excess of EDTA were added and the solution was boiled for 5 min. The solution was then cooled to approximately 50° and buffered to pH 3 5 with ammonium acetate. With NAS as indicator (Naphthyl Azoxine S)[7] the solution was then titrated just past the end-point with a standard copper solution and then titrated back to the red end-point with EDTA. The second end-point was sharper than the first, thereby justifying the double back-titration.

When large amounts of hydrochloric acid were present in the tin sample most of it was neutralized with sodium hydroxide before the solution was buffered In this case no additional sodium chloride was added.

If organic solvents were present in the tin sample, they were first removed by evaporation. A small amount of sulphuric acid was added to the sample to prevent volatilization of tin(IV) chloride. Small amounts of MIBK or IPE in the sample did not interfere with the titration.

When hydrofluoric acid was present, it was first removed by fuming with sulphuric acid in a platinum evaporating dish. The residue was then dissolved in 6*M* hydrochloric acid and transferred to a 250-ml beaker for analysis

Antimony(III) was determined by titration with standard potassium bromate, using α-naphthoflavone as indicator.[5] Antimony(V) was determined by the same procedure after reduction with sulphurous acid and boiling.

Mercury(II) was determined by titration with thioglycerol, using the thio analogue of Michler's ketone as indicator.[6] If an organic phase was present, it was rendered soluble by the addition of methanol; the final titration was performed in an aqueous methanol solution containing up to 50% v/v of methanol.

Cadmium, copper, lead and zinc ions were determined by titration at pH 5·5 with EDTA, NAS being used as indicator.[7] Bismuth was titrated directly at pH 2 with EDTA, Xylenol Orange being used as indicator. Molybdenum was determined gravimetrically as the 8-hydroxyquinolinate.[8]

Distribution ratios

Distribution ratios were obtained by shaking 20 ml of the aqueous phase containing a known amount of solute with 20 ml of the equilibrated organic phase. After equilibration in a separatory funnel, the phases were separated and one or the other (or both) was analysed for solute content. Because the phases were not pre-equilibrated, volume corrections were made where necessary.

RESULTS AND DISCUSSION

Distribution ratios

The degree of extraction and the distribution ratios for extraction of antimony(III) and (V), molybdenum(VI) and tin(IV) from aqueous hydrochloric acid into methyl isobutyl ketone (MIBK) are shown in Fig. 1. From approximately 6–8*M* hydrochloric acid, for all but antimony(III) there is a high degree of extraction. In Table I,

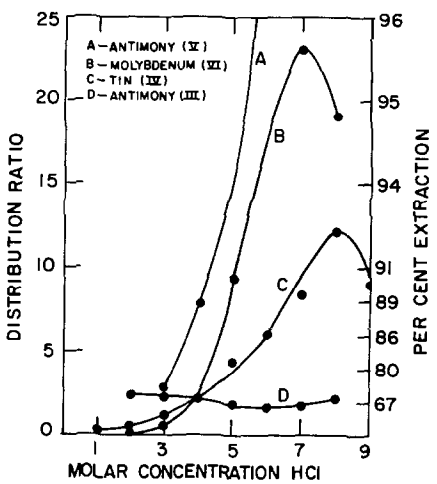

FIG. 1.—Distribution ratios for extraction of some metal ions from aqueous hydrochloric acid into MIBK.

data are given for batch extraction of several other elements known to form chlorocomplexes. These data indicate that a multistage partition technique should successfully separate tin(IV), antimony(V) and molybdenum(VI) from the other elements studied, as well as from a number of other metal ions known not to form chlorocomplexes readily or to be extracted into ketone solvents.

The effect of hydrofluoric and sulphuric acids on the extraction of tin(IV) and molybdenum(VI) from aqueous hydrochloric acid into MIBK was also studied (Table II). The data indicate that at relatively low concentrations of hydrochloric acid the extractabilities of both tin(IV) and molybdenum(VI) increase rapidly as the concentration of sulphuric acid is increased, and the extractability of tin increases

TABLE I —DISTRIBUTION RATIOS OF METAL IONS BETWEEN EQUILIBRATED MIBK AND HYDROCHLORIC ACID

Metal ion	Distribution ratio [HCl], *M*							
	1	2	3	4	5	6	7	8
Bi(III)	0 22	—	0 10	—	0 016	—	0 007	0 038
Cd(II)	—	0 014	—	—	0 06	—	—	0·95
Cu(II)	—	0 0071	—	—	0·023	—	—	0·090
Hg(II)	—	—	—	—	—	—	—	1·39
Pb(II)	—	—	—	—	—	0 021	0 024	0 068
Zn(II)	—	0 035	—	—	0 04	—	—	0·26

faster than that of molybdenum. Addition of hydrofluoric acid to the hydrochloric acid system lowers the extractability of both tin and molybdenum, by reducing the concentration of extractable chloro-complexes and increasing the concentration of non-extractable fluoro-complexes. The distribution ratios in Table II also show that the extraction of tin(IV) containing no chloride is negligible from 1–10*M* hydrofluoric acid. This is apparently in gross disagreement with one published report[9] claiming essentially 100% extraction of tin(IV) from hydrofluoric acid into another oxygenated organic solvent (ethyl ether).

Edwards and Voigt[10] studied the extraction of antimony(III) and (V) from aqueous hydrochloric acid into di-isopropyl ether. They found a distribution ratio of approximately 200 for antimony(V) from 6·5–8*M* hydrochloric acid; they reported the extraction of antimony(III) to be negligible under the same conditions. We obtained

TABLE II.—DISTRIBUTION RATIOS FOR EXTRACTION OF TIN(IV) AND MOLYBDENUM(VI) INTO MIBK

Molar conc of acid			Distribution ratio	
HCl	H_2SO_4	HF	Sn(1V)	Mo(VI)
0 5	3 0	0	3 04	0 05
0 5	6·0	0	52 5	15 9
1·0	0	0	0·18	0 003
1·0	3 0	0	6 6	0 59
1 0	6 0	0	68 6	30 1
3 0	0	0	1·12	0 54
3 0	0·5	0	—	1 21
3 0	1·5	0	—	5 52
3·0	3 0	0	25 5	20 6
7 0	0	0	8 4	22·9
7 0	1 0	0	10 8	—
0	0	1·0	0·009	—
0	0	5 0	0·006	—
0	0	10·0	0·012	—
3·0	0	0 0	1 12	0 54
3 0	0	1 5	—	0 11
3·0	0	3 0	0 06	0 07
7·0	0	0	8 4	22 9
7·0	0	1·0	5 6	—
7·0	0	2·0	5 3	7 1
7·0	0	4 0	—	4 8
7 0	0	6 0	—	2 8

a distribution ratio of 41 for extraction of antimony(V) from 8*M* hydrochloric acid into di-isopropyl ether, and distribution ratios of 0·006 for tin(IV), 3·3 for arsenic(III) and 0·12 for molybdenum(VI) under the same conditions. It has been shown by ultraviolet spectroscopy that solvated $HSbCl_6$ is the species extracted from 6*M* hydrochloric acid into di-isopropyl ether.[11]

Column separations

Theory. Separation of two substances by batch type solvent extraction requires that one substance be quantitatively extracted while the extraction of the other under the same conditions is essentially nil. Separations based on partition chromatography,

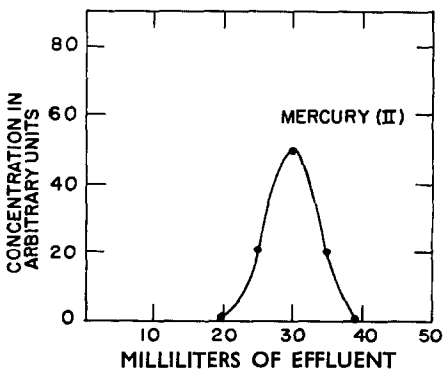

FIG. 2.—Curve for elution of 400 μmole of mercury(II) with 8*M* hydrochloric acid from a 25 × 1·3 cm Teflon-6 (160–170 mesh) column containing 12 ml of MIBK.

however, are feasible whenever there is merely a reasonable *difference* in the extractabilities of the two substances. Several successful separations of metal ions by reversed-phase partition chromatography have been reported by various workers.[12–14] In our work a special Teflon-6 was used to retain MIBK as the stationary phase, while an aqueous phase was used to introduce the sample and as the eluent to separate the substances on a column. Chromosorb W, treated with dichlorodimethylsilane to make it retain MIBK in preference to the aqueous phase, was also used but was found to be somewhat inferior to the Teflon-6.

If a separation proceeds by pure partition chromatography (*i.e.*, there is no adsorption or ion-exchange interaction between the solutes and the solid support), it can be shown that the following relationships exist between the batch distribution ratio, D, and the retention volume, V_r, when a solute is eluted from a column.

$$V_r = DV_s + V_m$$

where V_r is the retention volume, *i.e.*, the volume of eluent required for the eluted solute to reach its maximum concentration in the effluent; D is the batch distribution ratio for extraction of the solute from the aqueous to the organic phase; V_s is the volume of the stationary liquid phase (MIBK, for example); V_m is the volume of the mobile phase in the column (*i.e.*, the interstitial volume); all volumes are expressed in the same units (usually ml).

To test this equation, a sample of mercury(II) was eluted with 8*M* hydrochloric acid from a 25 × 1·3 cm column of 160–170 mesh Teflon-6 impregnated with MIBK (see Fig. 2). In this experiment $D = 1{\cdot}39$, $V_s = 10{\cdot}5$ ml and $V_m = 12$ ml. The

calculated V_r is 26·5 ml which is in reasonably good agreement with the experimental V_r of 30·0 ml. In this experiment the number of theoretical plates in the column was calculated from the relationship, $N = 8(V_r/\beta)^2$, where N is the number of theoretical plates and β is the width of the elution curve (in ml) at the concentration $c = c_{max}/e = (0{\cdot}368)c_{max}$. In this case N was found to equal 72 theoretical plates, corresponding to an HETP of about 3·5 mm.

Separation of tin(IV) and molybdenum(VI). The distribution ratios given in Table II indicate that the greatest separation factor for tin and molybdenum occurs where the sulphuric acid is 3*M* and the hydrochloric acid concentration ranges from 0·5 to

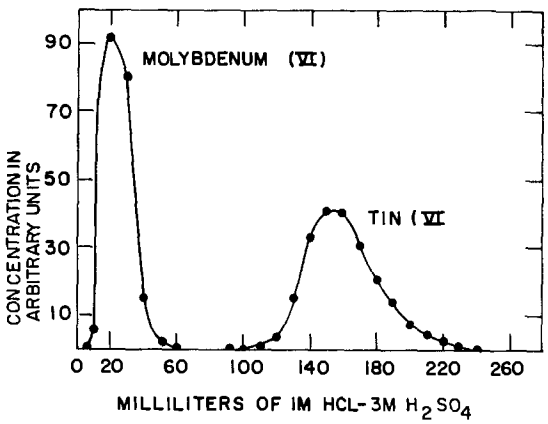

FIG. 3. Elution of 400 μmole each of molybdenum(VI) and tin(IV) from a 40 × 1 1 cm column of dichlorodimethylsilane-treated Chromosorb W impregnated with MIBK.

TABLE III.—SEPARATION OF TIN AND MOLYBDENUM

Metal ion	Added, *mmole*	Found, *mmole*	Error, %
Mo(VI)	0 3196	0·3203	+0 2
	0·3196	0 3186	−0 3
Sn(IV)	0·4498	0 4511	+0 3
	0 4498	0 4509	+0·2
	0·4498	0 4489	−0·2

1*M*. An eluent of 1*M* hydrochloric acid–3*M* sulphuric acid and a MIBK stationary phase was used for the separation. With this eluent a separation factor of 11 is obtained, and the distribution ratio of tin(IV) is sufficiently high for tin(IV) to be held on the column while the molybdenum(VI) is eluted.

An elution curve for the separation of approximately 400 μmole of tin and 400 μmole of molybdenum on a 40 × 1·1 cm column of 80–100 mesh Chromosorb W is given in Fig. 3. Results for quantitative separations are given in Table III.

Separation of tin(IV) from bismuth(III), cadmium(II), copper(II), mercury(II), lead(II) or zinc(II). A comparison of the distribution ratios for the metal ions given in Table I and those given in Fig. 2 for tin(IV) indicates the possibility of separating tin(IV) from every metal ion listed in Table I by reversed-phase chromatography with MIBK as the stationary phase and 8*M* hydrochloric acid as the mobile phase.

Although slightly more favourable separation factors can in some cases be obtained at somewhat lower acid concentrations, the equilibrium between the phases is more rapid at 8*M* hydrochloric acid than it is in the range from 3*M* to 7·5*M* acid.

For quantitative separations a 25 × 1·3 cm column of 160–170 mesh Teflon-6 impregnated with MIBK is employed. The less extracted element is eluted with 30 ml of 8*M* hydrochloric acid at a flow-rate of 2–3 ml/min. Mercury(II) has a higher distribution ratio ($D = 1{\cdot}39$) causing it to be held on the column longer; mercury is eluted in the 15–45 ml effluent fraction. After the elution with 8*M* hydrochloric acid is completed, tin(IV) is washed off the column with 20 ml of MIBK at 4–5 ml/min

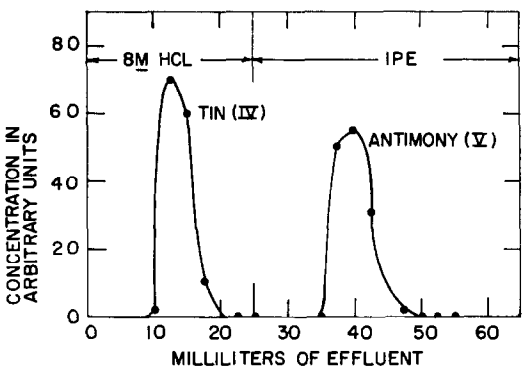

FIG. 4.—Elution of 400 μmole each of tin(IV) and antimony(V) with 8*M* hydrochloric acid from a 18 × 1·3 cm column of 160–170 mesh Teflon-6 impregnated with MIBK.

flow-rate. The column is now ready for the next sample. Quantitative results were obtained for the separation of binary mixtures of tin(IV) and each of the following: bismuth(III), cadmium(II), copper(II), lead(II), mercury(II) and zinc(II).

TABLE IV.—SEPARATION OF TIN AND ANTIMONY

Metal	Added, *mmole*	Found, *mmole*	Error, %
Sb(V)	0 3666	0 3666	+0 0
	0·3666	0 3656	−0 3
	0 3666	0 3681	+0 4
Sn(IV)	0 3911	0 3916	+0 1
	0·3911	0 3903	−0 2

Separation of tin(IV) and antimony(V). The distribution ratios of 41 and 0·006 for antimony(V) and tin(IV), respectively, from 8*M* hydrochloric acid into isopropyl ether indicate that a very effective separation should be possible by reversed-phase chromatography. Elution curves for the separation of approximately 400 μmole each of tin and antimony are given in Fig. 4. After complete elution of the tin(IV) with 8*M* hydrochloric acid, the antimony(V) is eluted with 30 ml of equilibrated isopropyl ether at a flow-rate of 5 ml/min. Continued elution with 8*M* hydrochloric acid would cause the antimony to appear after 50 ml of effluent had been collected. Quantitative results for separations are given in Table IV.

Zusammenfassung—Zinn(IV) wird durch Chromatographie mit umgekehrten Phasen auf einer Saule aus einem festen Trager, der mit einem organischen Losungsmittel beladen ist quantitativ von vielen anderen Metallionen getrennt. Mit waßriger 8*M* Salzsaure als Elutionsmittel wird Zinn(IV) auf einer mit Methylisobutylketon impragnierten Saule zuruckgehalten und quantitativ von Wismit(III), Cadmium(II), Kupfer(II), Blei(II), Quecksilber(II) und Zink(II) getrennt. Zur Trennung von Zinn(IV) und Molybdan(VI) dient als waßrige Elutionsphase 1*M* Salzsaure-3*M* Schwefelsäure. Eine mit Isopropylather beladene Saule halt Antimon(V) aus 8*M* Salzsaure quantitativ zuruck und gestattet rasche Elution von Zinn(IV).

Résumé—On sépare quantitativement l'étain (IV) de nombreux autres ions métalliques par chromatographie à phases inversées sur une colonne de support solide imprégnéd'un liquide organique. Lorsqu'on utilise l'acide chlorhydrique aqueux 8*M* comme éluant, l'étain (IV) est retenu sur une colonne imprégnée de méthylisobutylcétone et séparé quantitativement de bismuth (III), cadmium (II), cuivre (II), plomb (II), mercure (II) et zinc (II). Pour la séparation de l'étain (IV) et du molybdène(VI), la phase aqueuse éluante est l'acidechlorhydrique 1*M*-acide sulfurique 3*M*. Une colonne imprégnée d'éther isopropylique retient quantitativement l'antimoine (V) de l'acide chlorhydrique 8*M* et permet à l'étain (IV) d'être rapidement élué.

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STERIC HINDRANCE EFFECTS IN THE USE OF HETEROCYCLIC AZODYESTUFFS AS SPECTROPHOTOMETRIC REAGENTS

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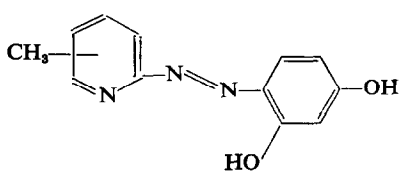
Summary—The heterocyclic azo dyestuffs 4-(*n*-methyl-2-pyridylazo)-resorcinol (where $n = 3', 4', 5', 6'$) have been prepared, and their possible use as spectrophotometric reagents investigated. The dyestuffs are shown to function analogously to the parent ligand 4-(2'-pyridylazo) resorcinol (PAR) in giving red complexes with the ions Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and UO_2^{2+}. Steric effects resulting from the position of the methyl group in the heterocyclic ring are shown to occur in relation both to the spectra of the dyestuffs themselves and to the sensitivity of their reactions with the metal ions.

SINCE the introduction of the reagent 1-(2'-pyridylazo)-2-naphthol (PAN) as a spectrophotometric reagent,[1] and the subsequent introduction[2] of the analogous compound 4-(2'-pyridylazo)resorcinol (PAR), the use of both of these reagents and of other heterocyclic azo dyestuffs for spectrophotometric purposes has now developed to the stage where analytical procedures for some 15 elements have been published. However, most of these methods are based on the determination of specified metals (see, *e.g.*, refs. 3–6), and there have been relatively few direct attempts to investigate the spectrophotometric sensitivity in terms of the structure of the reagent or the thermodynamic stability of the complexes formed.[7–9] As part of a programme to investigate such correlations we have prepared the methyl homologues of PAR (ligands I–IV), in which the methyl substituent is respectively in the 3-, 4-, 5-, and 6-positions of the heterocyclic ring. The spectra of the dyestuffs, and of their com-



I : 3-Me-PAR
II : 4-Me-PAR
III : 5-Me-PAR
IV : 6-Me-PAR

plexes with a series of bivalent metal ions have been obtained over a wide pH range. The absorbance–concentration curves have been investigated, and the spectrophotometric sensitivities of the reagents for the metal ions have been calculated.

EXPERIMENTAL

Preparation of ligands

Heterocyclic azo dyestuffs are usually obtained by the method of Tschitschibabin.[10,11] In this investigation it was found most convenient to prepare the ligands in the free base form rather than as the disodium salt. The appropriate 2-amino-methylpyridine (12 g) was dissolved in absolute ethanol (20 ml) and to this solution was added a solution of clean metallic sodium (2·4 g) in absolute ethanol (40 ml) followed by isoamyl nitrite (15·2 ml, 12 g). The solution was heated under reflux for 3-4 hr,

and the brown diazonium salt thus prepared was used directly without isolation. Resorcinol (14 g) was dissolved in water (20 ml), and to the solution was added the well-cooled suspension of the diazonium salt. The latter was always added to the resorcinol to prevent possible coupling of two molecules of diazonium salt with one of resorcinol. The resultant solution was allowed to stand for 48 hr, during which time the colour changed from the light brown of the diazonium salt to the dark brown-red of the dyestuff. The reaction mixture was diluted to 2 l. with water (it was found that if the alcohol content was greater than 5% the products were difficult to isolate), and then acidified to pH 4 5 with hydrochloric acid (8*M*). The flocculent precipitate so obtained was allowed to stand overnight, filtered, and thoroughly washed with water, in which resorcinol, the methylaminopyridines, and any sodium chloride formed in the acidification are soluble. Finally, after air-drying, the products were thoroughly washed with dry ether to remove any isoamyl nitrite. Analytical results are given in Table I.

TABLE I.—ANALYTICAL RESULTS FOR DYESTUFFS (FREE DYE FORMS)

Compound	C, %	H, %	N %	m p., °C
3-Me-PAR	63 0	5 0	18 1	170 (decomp.)
4-Me-PAR	63 1	4 9	18 2	192
5-Me-PAR	62 6	4 9	18 1	160
6-Me-PAR	62 3	4 9	18 2	162
Calc for Me-PAR	62 86	4 85	18 32	

Spectral measurements

All spectral measurements were made in matched 1-cm silica cells at room temperature, a Unicam SP 500 spectrophotometer being used. The range 340–520 mμ was covered in 5-mμ increments for the ligand spectra, and 450–620 mμ for the spectra of the complexes.

Reagents

All reagents were of reagent grade quality; sodium perchlorate was recrystallized before use. Because of the extremely high spectrophotometric sensitivity of the dyestuffs for metal ions, it was necessary to redistil distilled water from an all-glass still before use.

Procedures

Ligand spectra. Stock solutions of the dyestuffs (40 μg/ml) were prepared by direct weighing, known volumes of sodium hydroxide being added as required for dissolution of the free dye form. For 3-Me-PAR this concentration was found to be too low and an 80 μg/ml stock solution was used. Solutions for optical measurement were prepared by diluting 10 ml of the stock solution to 50 ml in graduated flasks, together with the appropriate quantities of buffer solutions (Clarke and Lubs[12], Sorenson and Walbum[13]) and sodium perchlorate to bring the ionic strength to 0 1. Measurements were made against blank solutions containing no dyestuffs over the pH range 1 6–12·5 at intervals of 0·6 pH unit. The pH was checked with a Cambridge pH-meter.

Spectra of complexes. The spectra were obtained for solutions prepared by mixing 10 ml of metal solution (10·00 μg M/ml), 2 ml of dyestuff solution (500 μg/ml) and 30 ml of buffer solution, and diluting to 50 ml in graduated flasks. The pH range covered was 5–10, and the ionic strength was 0·1. The solutions were measured against optical blanks prepared in the same fashion, but omitting the metal ion For the spectra of the uranyl complexes, which had a lower molar absorptivity, the overall uranyl concentration was increased five fold. Measurements were made 20 min after preparing the solutions, except in the case of the uranium complexes, for which it was found that the absorbance increased with time. After 24 hr it was found to be constant, and hence the uranium solutions were allowed to stand for this length of time before measurement. Random checks showed no detectable change in absorbance of the complexes over a period of 72 hr.

RESULTS AND DISCUSSION

Ligand spectra

Typical results are shown for 5-Me-PAR in Fig. 1. It is seen that it is possible to recognize the peaks due to each of the chromophoric species, namely the protonated dye H_3R^+, the free dye H_2R, and the anionic forms HR^- and $R^{=}$. The wavelengths of maximum absorption, and molar absorptivities are given in Table II. At the

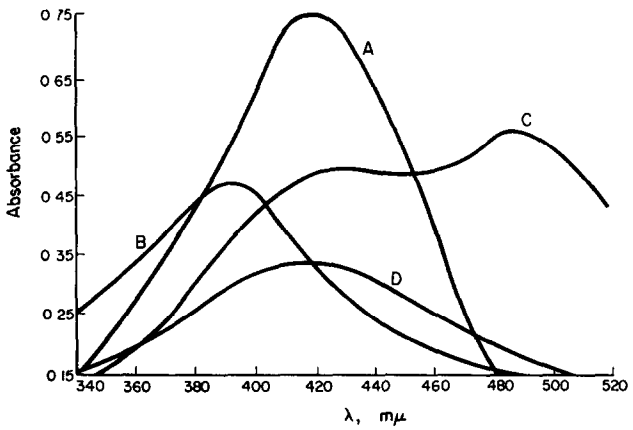


FIG. 1.—Spectra of absorbing species for 5-Me-PAR.
A = Mono-anionic form
B = Free dye form
C = Di-anionic form
D = Protonated form

TABLE II.—POSITION AND INTENSITY OF SPECTRAL BANDS

	3-Me-PAR		4-Me-PAR		5-Me-PAR		6-Me-PAR		PAR†	
	mμ	ε	mμ	ε	mμ	ε	mμ	ε	mμ	ε
Protonated	407*	6250	400	11930	420	13100	408	9400	395	15500
Free dye	407*	6050	392	11400	390	13650	397	8500	383	15700
Monoanionic	425	8025	417	17200	420	22230	416	12830	415	25900
Dianionic‡	492	4975	490	14900	490	14950	487	9075	485	17300

* Band much broader in acid solution, as for other isomers.
† Reference 9.
‡ Results for pH 12·5 (formation of dianionic form probably incomplete).

wavelength and pH of maximum absorption Beer's law is obeyed by all four absorbing species.

Spectra of complexes

Detailed spectra are not reproduced, but sensitivities at, and wavelengths of, maximum absorption and the pH of the solution are given in Table III.

TABLE III.—SPECTRAL DATA FOR COMPLEXES

Metal ion	3-Me-PAR			4-Me-PAR			5-Me-PAR			6-Me-PAR			PAR*
	λ	pH	sensitivity†	λ	pH	sensitivity†	λ	pH	sensitivity†	λ	pH	sensitivity†‡	sensitivity†
Cu	520	10	0 485	497	10	0 875	507	10	0 770	510	10	0 750	1 09
Co	528	9	0·512	507	8	0·925	517	9	0 800	520	8	1·00	0·980
Ni	510	9	0·650	495	10	1 13	507	10	1 13	505	8	1 03	1·21
Zn	515	10	0·775	495	9	1·16	500	9	1·17	505	10	1 42	—
UO_2	535	9	0 102	525	10	0 155	530	10	0 150	—	—	—	0·160

* From ref. 2.
† Absorbance/μg/ml.
‡ From linear part of plot.

It was found that for all complexes between the dyestuffs and nickel and zinc at pH values below 7·0 the complexes precipitated, and hence the absorbance could not be measured. For the uranium complexes there was no significant absorption in the visible region at pH less than 8·0.

Beer's law plots were obtained for all metal ions and dyestuffs used, at the pH and λ_{max} given in Table III. The stock solutions for this procedure were: dyestuff — 500 μg/ml, metal ion —10 μg/ml, except uranium — 50 μg/ml. The solutions had the compositions:

3-Me-PAR: 1 ml of dye solution + x ml of metal-ion solution (x = 0·2–1 0 ml, in increments of 0·2 ml) + 30 ml of buffer, diluted to 50 ml.

4- and *5-Me-PAR*: 2 ml of dye solution + x ml of metal-ion solution (x = 1·0–5 0 ml, in increments of 0 5 ml) + 30 ml of buffer, diluted to 50 ml.

6-Me-PAR: 2 ml of solution + x ml of metal-ion solution (x = 1·0–5 0 ml, in increments of 0 5 ml) + 30 ml of buffer, diluted to 50 ml.

All solutions were measured against a blank containing the appropriate quantity of buffer and dyestuff.

The Beer's law plots are linear over the concentration range given for 3-, 4-, and 5-Me-PAR, and for 6-Me-PAR are very shallow curves.

Acid dissociation constants

There have been many attempts to use spectral data for calculation of pK_a values of dissociable ligands, mainly based on the methods of Dyrssen,[14] Irving,[15] and Schwarzenbach.[16] However, these are normally applicable to systems with two widely separated dissociations; in the systems described here, there are at least three dissociations:

$$\text{protonated} \rightleftharpoons \text{free dye} \rightleftharpoons \text{mono-anionic} \rightleftharpoons \text{di-anionic}$$

with the possibility of further protonation in the most strongly acidic solutions. Although each of these species is recognizable from the spectra obtained, accurate pK_a values were not obtained, because of the complexity of the equilibria involved. Nevertheless, it is apparent from the range of pH values for which each species is present that $pK_{NH} \sim 3$, $pK_{(OH)_1} \sim 6$, and $pK_{(OH)_2} \sim 11$, in accordance with previous values for PAR and PAN,[7,9] but the values for 3-Me-PAR are about 1·5 units higher. It is well-known that in *o*-hydroxy azo dyestuffs there is intramolecular hydrogen bonding between the OH group and the adjacent azo nitrogen, giving a five-membered ring. This is considered[7,17] to account in part for the *p*-hydroxy group ionizing before the hydroxy group in PAR. There should be a greater spectral shift when the hydrogen-bonded OH group ionizes than for the *p*-OH ionization. Comparison of the measured shifts (Table IV) shows beyond doubt that the *p*-OH-group does ionize first, the shifts for the *o*-OH ionization being some 3–4 times as large. The intensities

TABLE IV.—BATHOCHROMIC SHIFTS IN SPECTRA OF DYESTUFFS

	3-Me-PAR mμ	4-Me-PAR mμ	5-Me-PAR mμ	6-Me-PAR mμ	PAR[9] mμ
Free dye → protonated	0	8	30	11	12
Free dye → mono-anionic	18	25	30	19	32
Mono-anionic → di-anionic	67	63	70	71	70

of the bands for all the dyestuffs are consistent, the order being mono-anionic > free dye ~ protonated; the di-anionic form does not fall into a regular pattern, probably because of the difficulty in obtaining the dyestuffs exclusively in this form. Intensities are uniformly lowest for the 3-methyl isomer, for which consideration of molecular models shows that there is considerable steric hindrance to the *trans* planar form

(methyl group *trans* to *o*-hydroxy) required for maximum delocalization and hence greatest intensity.

Consideration of the metal-dyestuff spectra shows a number of very interesting points. The order of molar absorptivities noted in the spectra of the dyestuffs alone is retained, the low values for 3-Me-PAR undoubtedly again being steric in origin. The complexes of 4-Me-PAR and 5-Me-PAR obey Beer's law over a much wider range of concentration than those of the other two isomers, the values for the 4- and 5-methyl isomers being close to those obtained for PAR. However, since these ligands are less easy to prepare than PAR, there does not seem to be any virtue in using these reagents instead of PAR for spectrophotometry. For 6-Me-PAR there is no measurable complex with the uranyl ion, presumably because of steric interactions, although with the other complexes the effect of the methyl group in the 6 position is small. The concentration range over which Beer's law applies exactly to the complexes of this ligand is rather restricted, though the very high sensitivity with zinc may well have analytical applications.

We are now engaged in the determination of the solution stoichiometries of the complexes of these ligands. Use of the mole ratio method has previously given unusual results with azo dyestuffs, apparent mole ratios of up to 4:1 dyestuff:metal being obtained for PAR,[2] in contrast to the potentiometric data which indicate only 1:1 and 2:1 complexes.[8,9] Other workers have obtained values of 8:1,[18] 15:1,[19] and in one case over 50:1.[20] With the ligands at present under investigation, apparent stoichiometries approaching 4:1 are obtained, and it appears that for complete colour formation a considerable excess of dyestuff is required.

Zusammenfassung—Die heterocyclischen Azofarbstoffe 4-(*n*-Methyl-2′-pyridylazo)resorcin (mit $n = 3',4',5',6'$) wurden dargestellt und ihre Anwendungsmoglichkeit als spektrophotometrische Reagentien gepruft. Es wird gezeigt, daß die Farbstoffe analog wirken wie ihre Muttersubstanz 4-(2′-pyridylazo)resorcin (PAR): sie geben rote Komplexe mit den Ionen Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} und UO_2^{2+}. Auf der Lage der Methylgruppe im heterocyclischen Ring beruhende sterische Effekte manifestieren sich sowohl in den Spektren der Farbstoffe selbst als auch in der Empfindlichkeit ihrer Reaktionen mit den Metallionen.

Résumé—On a préparé les colorants azo hétérocycliques 4-(*n*-méthyl 2′-pyridylazo) résorcinol (où $n = 3', 4', 5', 6'$) et étudié leurs possibilités d'emploi comme réactifs spectrophotométriques. On montre que ces colorants ont un comportement analogue à celui du ligand apparenté 4-(2′-pyridylazo) résorcinol (PAR) en donnant des complexes rouges avec les ions Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} et UO_2^{2+}. On montre que des effets stériques résultant de la position du groupe méthyle sur le noyau hétérocyclique se manifestent en relation tant avec les spectres des colorants eux-mêmes qu'avec la sensibilité de leurs réactions avec les ions métal liques.

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EXTRACTION OF REDUCED MOLYBDOSILICIC ACID AND ITS APPLICATION TO THE DETERMINATION OF TRACES OF SILICON

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Summary—It is difficult to find satisfactory organic solvents for the extraction of reduced molybdosilicic acid, but extraction is possible with isoamyl or isobutyl alcohol if the acid concentration of the aqueous solution is increased before the extraction, the best results being obtained by extraction with isoamyl alcohol from 3·5–4·5*N* sulphuric acid medium. This makes the reduced molybdosilicic acid method much more sensitive and permits the determination of microgram amounts of silicon in various kinds of high-purity metals.

THE reduced molybdosilicic acid method is very often used for the micro-determination of silicon but the reduced molybdosilicic acid is not extracted easily into organic solvents. Reduced molybdophosphoric acid, however, is easily extracted by organic solvents and can be separated in this way from reduced molybdosilicic acid, and phosphorus determined.[1] It has been reported that reduced molybdosilicic acid can be extracted into chloroform after addition of oxy-ethylated fatty amines to the aqueous solution.[2,3] We have found that reduced molybdosilicic acid can be extracted easily with isoamyl alcohol if the acid concentration of the aqueous layer is increased. Optimal conditions for the extraction have been established, and the method applied to the determination of microgram amounts of silicon.

EXPERIMENTAL

Solvent extraction of reduced molybdosilicic acid

Molybdosilicic acid can be reduced in various ways. We used reduction with iron(II) with hydrofluoric acid present to avoid the effect of phosphorus and arsenic, because these two methods have been generally used in the Japanese Industrial Standard Methods.[4]

Reagents

Standard silicon solution. After preliminary drying at 110° for about 1 hr, 0 2140 g of pure silicon dioxide was mixed with 1 g of anhydrous sodium carbonate, fused in a platinum crucible, and dissolved in water to make 500 ml of solution containing 200 μg of silicon per ml. This stock solution was diluted accurately 100-fold.

Hydrogen peroxide solution, 100-volume (1 + 1) and (1 + 29).

Sulphuric acid, 5, 12, 15 and 18*N*.

Ammonium paramolybdate tetrahydrate solution, 10% w/v.

Hydrofluoric acid (10 + 48).

Iron (II) ammonium sulphate solution, 15% w/v in sulphuric acid (1 + 9).

Tin (II) chloride solution, 10% w/v in 5*N* sulphuric acid, freshly prepared.

All reagents were stored in polyethylene bottles.

Procedure

A solution containing silicon was placed in a polyethylene separatory-funnel together with 1·7 ml of 5*N* sulphuric acid and was diluted to 25 ml Then 6 ml of ammonium molybdate solution were added and the mixture was allowed to stand at room temperature for 5 min.[4] After the addition of

7 ml of hydrofluoric acid (10 + 48), 5 ml of iron(II) ammonium sulphate solution were added within 30 sec and the solution was mixed. The colour produced is stable and constant from 30 sec to 1 hr after the addition of iron(II)[4]. After a few minutes, 1 ml of tin(II) chloride solution was added and mixed, and then 20 ml of 12*N* sulphuric acid were added. The solution was next shaken for about 30 sec with 10 ml of isoamyl alcohol to extract the reduced molybdosilicic acid. The organic phase was transferred to a dry test-tube, and then, after any water in it had become deposited on the wall of the tube, was transferred to a cuvette and its absorbance at 800 mμ was measured and corrected for the reagent blank. The absorption spectrum is shown in Fig. 1. Beer's law is obeyed, and the molar absorptivity is $18{\cdot}5 \times 10^3$. The calibration curve must be checked for each new batch of reagents.

Choice of solvent

The reduced molybdosilicic acid could not be extracted with benzene, chloroform or dichloroethane; it could be extracted with methyl isobutyl ketone but the colour was unstable. Extraction

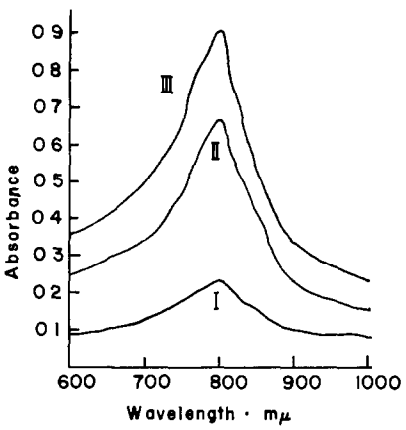

FIG. 1.—Absorption spectrum of reduced molybdosilicic acid in isoamyl alcohol.
I—Blank
II—1 μg of silicon/ml of extract
III—Blank plus 1 μg of silicon/ml of extract

with either isoamyl or isobutyl alcohol gave a colour stable for about 50 min, but the separation of the phases was more rapid with isoamyl alcohol, and this alcohol was therefore used subsequently.

Equilibrium time

It was found that shaking for 20 sec is sufficient to yield a constant absorbance for a fixed amount of silicon, and the extraction time was therefore set at 30–50 sec. If the shaking time is too long, the separation of the phases is slow and there tends to be more water in the organic phase.

Effect of acidity on the extraction and reduction

Reduced molybdosilicic acid cannot be extracted at the acidity needed for the reduction but it can be extracted easily with isoamyl alcohol if the acidity of the solution is increased. The optimal acidity range was determined by varying the amount of acid added; to avoid generation of heat, 12 or 15*N* sulphuric acid was added and the aqueous-phase was diluted to about 60 ml. Table I shows that the optimal acidity for extraction is 3·5–4·5*N* sulphuric acid.

Table II shows the effect of acidity on the reduction reaction, and shows that initial addition of 1·2–2·5 ml of 5*N* sulphuric acid does not affect the absorbance.

Effect of iron(III)

Iron(II) is used as the reducing agent and therefore the presence of iron(III) cannot be avoided. If the method is used for steel analysis, large amounts of iron(III) will be present. A solution containing 10 μg of silicon was carried through the procedure after the addition of 0·05 and 0·10 g of iron(III) sulphate. The absorbance was extremely low and it was observed that the blue colour became slightly pale on the addition of sulphuric acid before extraction. This was considered to be due to oxidation of the reduced molybdosilicic acid by iron(III) when the acidity was increased. Attempts to reduce the iron(III) to iron(II) showed that tin(II) chloride was the most suitable reductant.

The results in Table III indicate that this source of interference can be almost completely removed by reduction of the iron(III) with tin(II).

TABLE I.—EFFECT OF ACIDITY BEFORE EXTRACTION ON THE DETERMINATION OF 10 μg OF SILICON

Sulphuric acid, *N*	Absorbance of extract	
	Blank	Corrected for blank
1	0 070	0 155
	0·069	0 160
2	0·140	0·338
	0·140	0 332
3	0·200	0·570
	0 199	0 560
3 5	0·235	0 665
	0 234	0·670
4	0 235	0 667
	0·235	0·665
4·5	0·235	0·665
	0·235	0·667
5	0 221	0·660
	0·220	0 654

TABLE II.—EFFECT OF INITIAL AMOUNT OF SULPHURIC ACID ON COLOUR PRODUCED FROM 6·4 μg OF SILICON

5*N* H_2SO_4, *ml*	Absorbance of extract	
	Blank	Corrected for blank
1 0	0 268	0·420
	0·270	0·419
1·2	0·274	0·424
	0·271	0·429
1 5	0·274	0·425
	0 274	0·430
1 7	0·269	0 430
	0·272	0·421
2 0	0·270	0·425
	0·271	0·431
2·5	0 273	0·430
	0·272	0·427

TABLE III.—EFFECT OF IRON(III) ON THE DETERMINATION OF 10 μg OF SILICON

Fe^{3+} added, *g*	Absorbance of extract		
	Blank	Corrected for blank	Tin(II)
—	0·170	0·650	Not added
—	0·170	0·650	
0·05	0·045	0 111	Not added
0·05	0·045	0·109	
0·05	0·173	0 650	Added
0·05	0·173	0·648	
0·10	0 175	0·649	Added
0 10	0·175	0·648	

Iron(III) has another effect however, it is generally regarded as interfering in the production of the initial, unreduced, form of the heteropoly acid. The usual practice is to increase the amount of ammonium molybdate to prevent this interference. The effect of varying the amount of ammonium molybdate and iron(III) was studied, and the results are shown in Fig 2.

The effect of about 0 06 g of iron on the initial heteropoly acid formation can be prevented by the addition of 6 ml of 10% ammonium molybdate solution. This volume must be increased if iron is present in larger amount and the presence of 0 1 g of iron requires 12 ml of the molybdate solution.

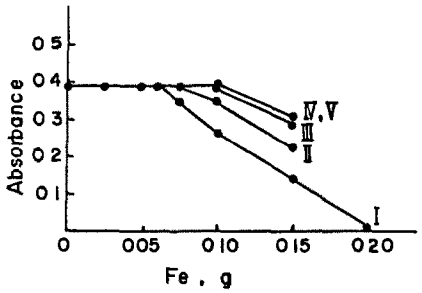

FIG. 2.—Interaction of iron(III) and ammonium molybdate in determining absorbance of 6 μg of silicon.
Ammonium molybdate solution added. I—6 ml, II—8 ml; III—10 ml; IV—11 ml; V—12 ml.

Effect of various ions

Sodium. Since sodium hydroxide is often used for the dissolution of the sample and for the neutralization of the sample solution, the effect of sodium sulphate formed from it was examined. As shown in Table IV, the presence of sodium sulphate up to 3 g (equivalent to 1 7 g of sodium hydroxide) had almost no effect.

Other ions. As shown in Table V, many of the ions examined showed no effect when present in amounts up to 125 mg (the maximum added) but some had a large effect even when present in small amount. Some of the ions are precipitated as their hydroxides or sulphates, and the amount actually present in the solution will be much lower than the amount shown. The extraction procedure has the advantage that the presence of precipitates does not affect the determination of silicon. As might be expected, the interference of germanium is positive and very large and cannot be prevented by the addition of hydrofluoric acid.

DETERMINATION OF MICROGRAM AMOUNTS OF SILICON

In iron and steel

Procedure. To 0·2 g of the sample, in a polyethylene beaker, add 8 ml of 5*N* sulphuric acid and 5 ml of hydrogen peroxide (1 + 1) and warm the beaker in a water-bath to effect dissolution. Continue the heating to decompose the excess of hydrogen peroxide and add 1*N* potassium permanganate dropwise until a faint pink colour persists. Decompose the excess of permanganate by dropwise addition of hydrogen peroxide (1 + 29), and heat the solution in a water-bath to decompose the excess of peroxide. Cool the solution and transfer it to a 100-ml standard flask, dilute it to the mark with water and mix it thoroughly. Transfer 25 ml of this solution by pipette to a polyethylene separatory-funnel, add 6 ml of ammonium molybdate solution (12 ml for a 0·4-g sample) and carry out the procedure described. The decomposition of hydrogen peroxide is difficult in the blank test and it is advisable to add exactly the same amount (about 20 mg) of iron with a low silicon content, to both the sample and the blank.

Calibration curve. Dissolve several 0·2-g pieces of iron with a low silicon content (or portions of an iron salt from which silicon has been removed) in 7 ml of 5*N* sulphuric acid and 5 ml of hydrogen peroxide (1 + 1), decompose the excess of peroxide, oxidize each of the solutions, and cool and transfer them to 100-ml standard flasks. To each of these solutions add a different amount of standard silicon solution, in the range 0–20 ml (0–40 μg of silicon), dilute them to the mark with water and mix. Take 25 ml of each solution through the procedure and plot the absorbance against the amount of silicon.

In manganese

Procedure. To 0·2 g of the sample, in a polyethylene beaker, add 5 ml of water and 8 ml of 5*N* sulphuric acid (10 ml for 0·4 g of sample). When the reaction has subsided, warm the beaker on a

TABLE IV.—EFFECT OF SODIUM SULPHATE ON THE DETERMINATION OF 5 μg OF SILICON

Sodium sulphate added, *g*	Absorbance of extract	
	Blank	Corrected for blank
0	0·280	0 326
	0·279	0·327
0·5	0 280	0·327
	0·280	0·327
1·0	0·279	0 327
	0 280	0·326
2·0	0·279	0·327
	0 278	0·327
3·0	0·278	0 327
	0 279	0·326
5·0	0·260	0 320
	0·260	0·318
7 5	0 253	0·305
	0·252	0·307
10·0	0·220	0 275
	0·220	0·273

TABLE V.—EFFECT OF VARIOUS ELEMENTS ON THE DETERMINATION OF 4 μg OF SILICON

Element added	Limit of tolerance,* *mg*	Remarks
Al, Mn, Mg, Zn, Cu, Co, Ni, Cd, Be	125	
Cr	75	
W	50	WO_3 precipitated, re-dissolved by HF
Sn, Ce, V	25	Hydrolysis
Bi, Nb, Ta		Hydrolysis
Ca		$CaSO_4$ precipitated
Hg, Ag		Reduced to metal by $SnCl_2$
Pb	10	$PbSO_4$ precipitated
Ti		Hydrolysis
Sb	5	Hydrolysis
Te		Reduced to metal by $SnCl_2$
As		
P	0·3	
Ge	0·0001	

* Tolerance limit is amount that causes an error of $<1\%$ in the absorbance.

water-bath to complete the dissolution. Add 1*N* potassium permanganate dropwise until a faint pink colour persists, transfer the solution to a 100-ml standard flask and dilute it to the mark with water. Transfer exactly 25 ml of this solution to a polyethylene separatory-funnel, add 6 ml of ammonium molybdate solution, and apply the extraction procedure as before.

Calibration curve. Place 0–20 ml volumes of standard silicon solution (0–40 μg of silicon) in 100-ml standard flasks, add 6 ml of 5*N* sulphuric acid to each, and dilute to the mark with water. Take 25-ml portions of these solutions through the procedure and plot absorbance *vs.* amount of silicon.

In magnesium

Procedure. To 0·2 g of the sample, in a polyethylene beaker, add 10 ml of water, 2 ml of saturated boric acid solution, and then 8 ml of 5*N* sulphuric acid (add an extra 1·5 ml of acid for each extra 0 1 g of sample) in small portions. The boric acid does not affect the final extraction or the results. When the reaction has subsided heat the beaker in a water-bath to complete the dissolution. Apply the permanganate oxidation and the rest of the procedure as described for manganese.

In aluminium

High-purity aluminium is difficult to dissolve in acid and sodium hydroxide is used as solvent. However, a large quantity of sodium hydroxide is one of the main sources of a high blank value and also affects the colour produced. Consequently, the amount of sodium hydroxide added was minimized, although this necessitated a longer time for the dissolution.

Procedure. Dissolve 0 2 g of the sample in 5 ml of 5*N* sodium hydroxide and 5 ml of water in a polyethylene beaker by letting the mixture stand overnight at room temperature. If necessary, warm the beaker to complete the dissolution. Add 12 ml of 5*N* sulphuric acid and warm in a water-bath to dissolve the aluminium hydroxide formed. Continue as for magnesium

In sodium hydroxide

Procedure. To 0 5 g of sodium hydroxide in a polyethylene beaker, add 8 ml of 5*N* sulphuric acid (add another 1 ml for each extra 0·2 g of sodium hydroxide) and carry through the procedure for magnesium. The maximum permissible size of sample is about 1·5 g.

RESULTS AND DISCUSSION

To check the precision and bias of results, samples of steel, iron, manganese, magnesium, magnesium alloys, aluminium and sodium hydroxide were analysed by the proposed methods.

The within-batch standard deviation of blank determinations was 0·13 μg of silicon. Thus,[5,6] the limit of detection was approximately 0·3 μg of silicon, *i.e.*, 0·00015% silicon in a 0·2-g sample.

Each sample (except sodium hydroxide) was also analysed by an independent method (gravimetric or absorptiometric). The silicon contents of these samples varied from 0·0003 to 0·012%, and in no case did the results of the two methods differ by more than 0·005% for the same sample; the differences were usually much smaller. The coefficients of variation ranged from 2 to 8%. Some typical results are given in Table VI.

Reduced molybdosilicic acid is shown to be completely extractable with isoamyl alcohol if the acid concentration is high enough. This means that the sensitivity of the method can be increased. By the normal non-extractive method the lowest limit

TABLE VI

Sample	Si% (Mean of six results)	Standard deviation, %	Coefficient of variation, %
Steel	0 00225	0·000083	3·7
Iron (electrolytic)	0 00055	0·000046	8 3
Manganese (electrolytic)	0·00138	0·000054	3·9
Magnesium (high-purity)	0·00212	0·000075	3·5
Magnox	0·00360	0·000055	1·5
Aluminium	0·00542	0·000079	1·5
Aluminium (high-purity)	0·00116	0·000049	4·2
Sodium hydroxide	0 00196	0 000062	3 2

for the determination of silicon is about 0·002% in a 0·2 g sample. This can be lowered to about 0·0002% by the method proposed here, but the blank values tend to become larger. Since the blank value is generally due to the reagents and water used, water and reagents yielding the smallest possible blank values must be selected, and a correction applied for the blank. If samples are dissolved in glass beakers there is a very high blank value due to the glass, the values often become inconstant, and the determination itself becomes impossible. For this reason a polyethylene beaker must be used.

Zusammenfassung—Es ist schwierig, zur Extraktion reduzierter Molybdokieselsaure ausreichende organische Losungsmittel zu finden. Die Extraktion mit Isoamyl- oder Isobutylalkohol ist jedoch moglich, wenn die Saurekonzentration der waßrigen Losung vor der Extraktion erhoht wird. Die besten Ergebnisse erhält man durch Extraktion mit Isoamylalkohol aus 3,5–4,5*N* schwefelsaurer Lösung. Dadurch wird die Analysenmethode mit reduzierter Molybdokieselsaure viel empfindlicher und gestattet die Bestimmung von Mikrogrammengen Silicium in verschiedenen Arten hochreiner Metalle.

Résumé—Il est difficile de trouver des solvants organiques satisfaisants pour l'extraction de l'acide molybdosilicique réduit, mais l'extraction est possible avec les alcools isoamylique ou isobutylique si la concentration en acide de la solution aqueuse est augmentée avant l'extraction, les meilleurs résultats étant obtenus par extraction à l'alcool isoamylique à partir d'un milieu 3,5–4,5*N* en acide sulfurique. Ceci rend la méthode à l'acide molybdosilicique réduit beaucoup plus sensible et permet le dosage de quantités de silicium de l'ordre du microgramme dans diverses espèces de métaux de haute pureté.

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STUDIES IN ATOMIC-FLUORESCENCE SPECTROSCOPY—III*

MICROWAVE-EXCITED ELECTRODELESS DISCHARGE TUBES AS SPECTRAL SOURCES FOR ATOMIC-FLUORESCENCE AND ATOMIC-ABSORPTION SPECTROSCOPY

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Summary—Details are given for the production and operation of microwave-excited electrodeless discharge tubes for use as sources in atomic-fluorescence and atomic-absorption spectroscopy. Special reference is made to the tubes for selenium and tellurium and their spectral characteristics are fully discussed. Optimum conditions are given for producing suitably intense and stable sources.

HOLLOW-CATHODE lamps have been used almost exclusively as spectral sources in atomic-absorption spectroscopy since the introduction of the technique by Walsh.[1] Although they have served their purpose well, they possess a number of undesirable features. They have only a relatively short "shelf-life", they are expensive, especially if a large number of elements is to be examined, and they require a "warm-up" period before use. Also, hollow-cathode lamps are difficult to produce for some elements, and for others the intensity is too low to give a sufficiently sensitive determination or a wide enough working range. The recent introduction of multi-cathode and high intensity lamps overcomes some of these problems, but only at the expense of others; for example selective volatilization of the more volatile elements and increased cost. Lastly, the necessary equipment required to produce hollow-cathode lamps means that the average user must rely largely on commercially available lamps.

Spectral discharge lamps have also been recommended,[2] but there is only a limited number commercially available and these sources are often self-reversed to an appreciable extent. The application of a continuous source[3] is also possible, but only in conjunction with a high resolution monochromator.

For the purpose of atomic-fluorescence spectroscopy, intense sources are required because the analytical signal varies linearly with the source intensity at the wavelength of excitation. Spectral discharge lamps and a xenon arc (continuous) source have been used by both Winefordner *et al.*[4,5] and ourselves.[6,7] However, the spectral discharge lamps suffer from the disadvantages outlined above, and the intensity of a continuous source at any one wavelength, especially in the ultraviolet region, is very low. The use of electrodeless discharge tubes excited by microwaves would seem to be an obvious solution to spectral source problems in both atomic-absorption and atomic-fluorescence spectroscopy. They are known to give very sharp and intense spectral lines and they can be easily made with the minimum of equipment. Some

* Part II—R. M. Dagnall, K. C. Thompson and T. S. West, *Anal. Chim. Acta*, 1966, **36**, 269.

commercially available tubes have been used by Winefordner *et al.*[8] for atomic-fluorescence studies and Goodfellow[9] has made some measurements using an experimental type of microwave discharge source powered by a 2450 Mc/s magnetron unit. The production of some selected electrodeless discharge tubes for spectroscopic standardization experiments has been recently described by Steers.[10] However, up till the present time, the production of independent electrodeless discharge tubes solely for use as sources for atomic-absorption or atomic-fluorescence does not appear to have been discussed.

This communication surveys the essential steps that must be taken to produce electrodeless discharge tubes which are suitable as sources for both atomic-absorption and atomic-fluorescence spectroscopy. The development of two tubes, for selenium and for tellurium, is discussed in detail.

PREPARATION OF ELECTRODELESS DISCHARGE TUBES

The discharge tubes were made from transparent quartz tubing (Jencons Ltd.) of 8 mm internal diameter and 1 1 mm wall thickness. The vacuum line used was very simple and consisted of a two-stage rotary pump, a cold-trap, a means of introducing argon from a gas bulb, six B-10 outlets and a vacuostat (10^{-2}–10 torr), *cf.* Fig. 1.

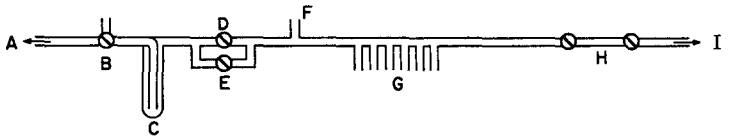

FIG. 1.—Vacuum line for preparation of microwave-excited source tubes.

A	Two-stage rotary pump	B	Three-way tap
C	Cold-trap	D	Two-way tap
E	Capillary leak	F	Vacuostat gauge
G	B10 connections	H	Two-way taps
	I Argon bulb.		

A 15–20 cm length of quartz tubing was sealed at one end and a constriction made between 1 and 7 cm from this end to give a tube from 1 to 7 cm in length. The tubing was then connected to a B-10 glass socket with medium-pressure tubing and the whole was attached to one of the outlets on the vacuum line and pumped down to a pressure of approximately 0·1 mm Hg. Argon was then introduced into the system after which it was again pumped down to a similar pressure. The quartz tube was then heated to just below its melting point for about 5 min, during which time argon was again introduced into the system and pumped out.

This procedure was found to be adequate for degassing the quartz. Other workers[11,12] have degassed their apparatus for up to 8 hr, but this was normally for the purpose of obtaining very "pure" spectra.

The tube was allowed to cool under vacuum and was then removed from the line. Between 5 and 20 mg of the required substance or substances were introduced into the tube which was then reconnected to the vacuum line.

The amount of substance used was found not to be critical, but too large a quantity sometimes caused plating-out during running.

The tube was evacuated as before, flushed out with argon and re-evacuated to a pressure of about 0·1 mm Hg. Gentle heat, depending on the volatility of the substance, was then applied to the tube to drive off any moisture or occluded gases in the substances used. The system was flushed twice more with argon and finally a given pressure of argon, depending on the substances used, was introduced into the vacuum system and the constriction was sealed by means of an oxy-propane hand torch.

In some instances tubes were sealed under as low a pressure as could be achieved whilst being continuously pumped. By such techniques, well over 150 tubes have been prepared for over 30 elements, *viz.*, Ag, Al, Ar, As, Bi, Cd, Co, Cr, Cu, Fe, Ga, Ge, H, Hg, I, In, Mg, Mo, N, Nb, Ni, P, Pb, S, Sb, Se, Sn, Te, Ti, Tl, V, Zn, Zr.

The following paragraphs describe in detail the preparation of discharge tubes for selenium and tellurium. Excitation of the tubes is achieved with a "Microtron 200" high-frequency generator and a

model 214.L. discharge cavity (Electro-Medical Supplies). The output frequency is 2450 ± 25 Mc/s (12·5 cm) at up to 200 W and the discharge cavity has external dimensions of approximately 2·5 cm diameter and 6 cm length with variable coupling at right-angles to the longitudinal axis of the cavity. The coaxial input connector is integral with cooling air inlets and the tuning stub is in line with the axis of the cavity. Initiation of the discharge is obtained with a Tesla coil vacuum-tester.

DISCHARGE TUBE CHARACTERISTICS

Selenium

Selenium tubes were made by introducing *ca.* 10 mg of analytical-grade selenium powder into the tubes and sealing off under various pressures of argon between 0·1 and 5·0 mm Hg. The selenium lines appeared to increase in intensity with decreasing argon pressure. The most intense selenium source used in this study was made by sealing whilst pumping, giving a final argon pressure of *ca.* 0·1 mm Hg. If the pressure was higher than 1 mm Hg the selenium lines were relatively weak and often the light blue selenium discharge would change over to a purple argon discharge with considerable reduction in the selenium line intensity. This particular tube required slight warming before initiation with the Tesla coil vacuum-tester, and was initially "run in" for about 2 hr. It is essential that all discharge tubes be "run in" because their characteristics can alter radically during the first hour of life. The tube required careful tuning and had to be moderately cooled to obtain a steady intense output. After continuous running of the selenium tube at 40 W for over 2 hr its stability was comparable with that of a hollow-cathode lamp, once the tuning and the cooling rate had been carefully adjusted.

All the expected selenium lines were observed during its operation and all of them were very sharp. The relative intensities of the ground state and intercombination lines observed, expressed as the ratio of the line intensity to that of the 1961 Å line, are shown in Table I.

These intensities can only be taken as an approximate guide because the values given are slightly dependent on the scanning rate of the Unicam SP 900A recorder unit. The relative intensity of the 1961 Å line increases with cooling. This suggests that, if the tube were run at too high a temperature or at energies >40 W, self-reversal of the resonance line might occur. On the other hand, when the tube was cooled too rapidly the discharge was extinguished. Uncooled tubes were not examined because the cavity tended to overheat. The apparently low intensity of the 1961 Å line is due to the characteristics of the 9601B photomultiplier used. This photomultiplier has a Corning U.V. glass window which has a very low transmission below

TABLE I.—EMISSION LINES FROM SELENIUM SOURCE

Line, *A*	Relative intensity	
	Slight cooling	Moderate cooling
1961 (*R*)	1	1
2040 (*R*)	5	2 5
2063 (*R*)	12	2
2075 (*I*)	3	5 0
2165 (*I*)	8	2·3

R ≡ Resonance; *I* ≡ Intercombination.

2000 Å. This illustrates one advantage of atomic-fluorescence measurements over atomic-absorption. Although the photomultiplier is very insensitive to the exciting radiation at 1961 Å or to emission at the same line, measurement may be made of the fluorescence at the 2040 Å "direct" line where a much increased response is given. This arises despite the suspected lower output of the source at 2040 Å. The selenium tube also emitted the mercury spectrum because of the diffusion of mercury from the vacuostat gauge throughout the vacuum system. Although it was found virtually impossible to eliminate this contamination completely, no resulting interference was observed.

Selenium tubes were made ranging from *ca.* 1·5 to 5·0 cm in length. The optimum length of tube for the cavity appears to be 3·5 cm. The smaller tubes were completely enclosed by the cavity and these developed hot-spots (selenium is a semiconductor) with the result that the output was neither very stable nor intense. The larger tubes did not reach a high enough running temperature to give a sufficient vapor pressure of selenium. The 3·5-cm tube was operated in such a manner that 1 cm of the tube protruded above the cavity and the selenium was sublimed to the top of the tube before operation, by heating gently with a Bunsen burner. This tube gave a steady, intense output. No information is at present available on tube-life because none of the tubes made to date has failed, even after *ca.* 50 hr of operation.

Tellurium

Tubes containing only tellurium metal were found to be unsatisfactory because they had to be run at high energies (*ca.* 75 W) and at relatively high temperatures owing to the involatility of tellurium. This resulted in a rather unstable output with eventual darkening of the quartz envelope.

A tube containing a trace of mercury plus tellurium gave a stable output but of low intensity. However, a tube containing tellurium and iodine (about 5 mg of each) which was sealed under continuous pumping (final argon pressure *ca.* 0·1 mm Hg) and run with slight cooling, gave a stable intense output at 30 W after an initial running-in period of 1 hr. The running-in period was necessary to allow complete reaction of tellurium and iodine under these low-pressure conditions.

All the expected tellurium lines were observed and, as with the selenium tube, were very sharp. Table II shows the intensities of the tellurium resonance and intercombination lines observed, relative to the intensity of the 2143 Å line. The iodine spectrum was also present in the form of a continuum with an intense line at 2062 Å.

As with selenium, the relative intensities are somewhat dependent on the rate of

TABLE II.—EMISSION LINES FROM TELLURIUM SOURCE

Line, Å	Relative intensity (slight cooling)
2143 (*R*)	1
2383 (*R*)	2 5
2386 (*R*)	4
2259 (*I*)	10
2531 (*I*)	1 3

recorder scanning and on the cooling rate. An increase in the operating power did not increase the line intensity appreciably, but merely led to instability.

The optimum tube length was found to be about 4 cm and the tube was best operated with about 1·5 cm protruding above the top of the cavity. After some 25 hr of intermittent running there has been no deterioration in output or stability.

Acknowledgements—We are grateful to the Science Research Council for the award of a research studentship to one of us (K. C. T.) and to I.C.I. Ltd for the award of a grant for the purchase of the Unicam SP 900A spectrometer used in these studies.

Résumé—On donne des détails sur la production et la manipulation de tubes à décharge sans électrodes excités par micro-ondes pour leur emploi comme sources dans la spectroscopie de fluorescence atomique et d'absorption atomique. On mentionne particulièrement les tubes pour le sélénium et le tellurium et discute de façon approfondie de leurs caractéristiques spectrales. On donne les conditions optimales pour la production de sources convenablement intenses et stables.

Zusammenfassung—Es werden Einzelheiten uber Herstellung und Arbeitsweise von mit Mikrowellen erregten elektrodenlosen Entladungsrohren als Lichtquellen bei der Atomfluoreszenz- und Atomabsorptionsspektroskopie mitgeteilt. Es wird besonders auf Selen- und Tellur-Rohren eingegangen und deren spektrale Eigenschaften voll durchdiskutiert. Die optimalen Bedingungen zur Herstellung geeignet intensiver und stabiler Lichtquellen werden angegeben.

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STUDIES IN ATOMIC-FLUORESCENCE SPECTROSCOPY—IV*

THE ATOMIC-FLUORESCENCE SPECTROSCOPIC DETERMINATION OF SELENIUM AND TELLURIUM

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Summary—Selenium and tellurium are determined down to 0·25 and 0·12 p.p.m. respectively by measuring the atomic-fluorescence signals at 2040 Å and 2143 Å respectively. Other possible wavelengths of measurement are considered in detail and the effects of some extraneous ions are examined. Microwave-excited electrodeless discharge tubes are used as spectral sources and intensity measurements are made with a Unicam SP 900A atomic-absorption/flame-emission spectrophotometer. Atomic-absorption measurements are also made with the same sources and spectrophotometer. The advantages of atomic-fluorescence methods and the use of electrodeless discharge tubes are discussed.

IN comparison with that for other elements, the volume of literature available on the flame-spectrophotometric determination of selenium and tellurium is relatively small. Rann and Hambly have determined selenium by atomic-absorption spectroscopy, using a hollow-cathode lamp and an electrodeless discharge tube operated at 15 Mc/s.[1] The limit of detection at 1961 Å was 1 ppm. A determination using a continuous source[2] and a medium quartz spectrograph gave limits of detection for selenium (2040 Å) and tellurium (2143 Å) of 5 and 0·5 ppm respectively. In addition to these, Dean[3] has described a flame-emission method for tellurium, using an oxy-acetylene flame. The tellurium(IV)–diethyldithiocarbamate complex was extracted into carbon tetrachloride, evaporated to dryness and redissolved in methyl isobutyl ketone to enhance the flame temperature. The limit of detection was 2 ppm.

This communication describes the determination of selenium and tellurium by atomic-fluorescence and atomic-absorption spectroscopy under conditions which do not require a hot flame, a high-resolution monochromator or hollow-cathode lamps. The oxidation state of the selenium and tellurium is unimportant and a preliminary extraction into organic solvents is unnecessary.

Spectral characteristics

The general theory of atomic-fluorescence has been described by Winefordner,[4] together with the determination of zinc, cadmium and mercury. The resonance lines of these elements originate from a $^1S_0$ ground state which is a singlet. However, for sulphur, selenium, tellurium and polonium[5] the ground state $^3P_2$ is part of the triplet $^3P_2$ $^3P_1$ $^3P_0$ (*cf.* Fig. 1) The separation of these states is very small (*cf.* Table I) and in tellurium and polonium the ^3P terms are partially inverted.

* Part III—R. M. Dagnall, K. C. Thompson and T. S. West, *Talanta*, 1967, **14**, 551.

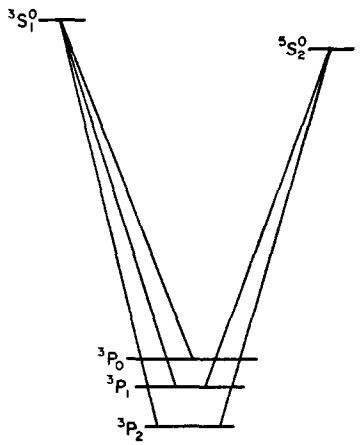

FIG. 1—Simplified Grotian diagram for S, Se, Te.

TABLE I.—SEPARATION OF GROUND STATES

Element	Interval, cm^{-1} $^3P_2 - {}^3P_1$	$^3P_1 - {}^3P_0$
S	398	174
Se	1989	545
Te	4751	−44
Po	16831	−9317

(1 eV = 8066 cm^{-1})

TABLE II —SPECTRAL RESONANCE LINES

Element	Transition, Å $^3P_2 \rightarrow {}^3S_1^0$	$^3P_1 \rightarrow {}^3S_1^0$	$^3P_0 \rightarrow {}^3S_1^0$
S	1807	1820	1826
Se	1961	2040	2063
Te	2143	2386	2383
Po	2450	4170	3003

Table II shows the spectral resonance lines which can be used for fluorescence measurements. It was found that the intercombination lines ($^3P_2 \rightarrow {}^5S_2^0$ and $^3P_1 \rightarrow {}^5S_2^0$) gave no appreciable absorption or fluorescence for any of these elements (*cf.* zinc, cadmium and mercury).

The resonance lines for sulphur lie in the vacuum-ultraviolet outside the range of the monochromator of the instrument used. For this reason it was not possible to make any fluorescence or absorption measurements for sulphur in the present study. With selenium, the 1961 Å and 2040 Å lines both absorb strongly whilst the 2063 Å line absorbs only very weakly. The 1961 Å line emanating from the ground state absorbs about 5 times as strongly as the line emanating from the $^3P_1$ state which lies 0·25 eV above the ground state. For tellurium the resonance line at 2143 Å absorbs almost 10 times as strongly as the lines at 2386 and 2383 Å. The $^3P_0$ and $^3P_1$ states lie 0·6 eV above the $^3P_2$ ground state

Atomic fluorescence was observed for selenium and tellurium for all three lines emanating from the $^3S_1$ state. However only very slight fluorescence was obtained for the intercombination lines for tellurium and none at all for those of selenium. The fluorescence for the transition from the $^3S_1$ excited state to the $^3P_{0,1,2}$ states is probably due to direct-line fluorescence; that is, excitation with the lines at 1961 and 2143 Å for selenium and tellurium respectively, with emission of selenium lines at 2040 and 2063 Å and of tellurium lines at 2386 and 2383 Å. Resonance fluorescence (excitation and emission wavelengths the same) is a possibility since some of the atoms could be thermally excited to the metastable $^3P_1$ and $^3P_0$ states. However, as the resonance lines for selenium and tellurium respectively absorb 5 and 10 times as strongly as the next highest states, and the energy gaps between the ground states and the next highest states of selenium and tellurium are 0·25 and 0·60 eV respectively, direct-line fluorescence seems much more probable. This aspect was not examined further because a monochromomator placed in front of the source would give a signal too weak to measure.

EXPERIMENTAL

Apparatus

The apparatus used consisted of a Unicam SP 900A atomic-absorption/flame-emission spectrophotometer coupled to a Honeywell-Brown 0–10 mV recorder. A description of its use for atomic-fluorescence measurements has been given elsewhere.[6] Electrodeless discharge tubes were prepared and used as sources and the discharge was maintained with a "Microtron 200" high-frequency generator and a model 214.L. discharge cavity (Electro-Medical Supplies).[7] The "emission" mode of operation of the Unicam SP 900A was used for all fluorescence measurements since this pulses the flame emission at 100 c/s in phase with the a.c. amplifier of the SP 900A. This does, however, result in the recognition by the detector of all radiation effects in the flame at the selected waveband. For this reason it would be better to modulate the light from the source mechanically or electronically before it enters the flame and to use the SP 900A in its "absorption" mode so that continuous radiation from the flame is not recorded by the detector/amplifier system. The basic instrumental arrangement for atomic-fluorescence measurements is shown diagrammatically in Fig. 2.

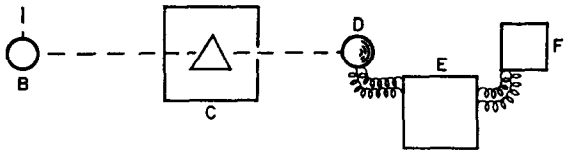

FIG. 2—Experimental arrangement for atomic-fluorescence measurements
A—Source B—Flame
C—Monochromator D—Photomultiplier
E—Amplifier F—Recorder

Stock solutions

Selenium solution (1250 *ppm*). Analytical-reagent grade selenium metal (1·250 g) was dissolved in 20 ml of a mixture of concentrated nitric and hydrochloric acids (1 + 1) and diluted to about 500 ml with distilled water. A slight excess of ammonia was then added and the whole was diluted to 1 l.

Tellurium solution (1250 *ppm*). Made up with analytical-reagent grade tellurium metal as for the selenium solution.

Both solutions were then diluted as required.

Atomic-Fluorescence Measurements

An air–propane flame was used because of its low background emission[6] and the discharge cavity was placed *ca.* 8 cm from the flame at right-angles to the optical axis of the analysing monochromator. Slit-widths ranging from 0 5 to 2 0 mm were used. The excitation sources were not chopped and so

any flame background had to be subtracted arithmetically from the readings obtained. A slightly fuel-rich flame was used and the distance from the top of the propane emission-burner head to the centre of the analysing monochromomator slit was *ca.* 3 cm. The atomic-fluorescence intensity was virtually independent of flame composition and position of measurement in the flame for both selenium and tellurium.

Selenium

The discharge tube was operated at 40 W with moderate cooling and fluorescence measurements were taken at the resonance lines (1961, 2040 and 2063 Å) and the intercombination lines (2075 and 2165 Å), with a 12·5-ppm solution of selenium. The recorder readings due to the fluorescence emission are shown in Table III together with the relative line intensities.

TABLE III.—FLUORESCENCE INTENSITIES FOR SELENIUM

Wavelength, *Å*	Recorder reading	Relative line intensity (source)
1961	42	1
2040	63	5
2063	33	12
2075	1	3
2165	0	8

The 1961 Å resonance line is the strongest fluorescing line, but because the photomultiplier used (EMI 9601B) is very insensitive below about 2000 Å, the 2040 Å line gives the higher readings. The latter wavelength was used for further measurements.

Linear calibration curves were obtained over the range 0·25–125 ppm of selenium, with a slit-width of $<2{\cdot}0$ mm. More concentrated solutions were not examined. The limit of detection (signal to noise ratio unity) was 0·15 ppm and the limit of measurement was considered to be *ca.* 0·25 ppm (*i.e.*, twice the background signal).

Tellurium

The discharge tube was run at 30 W with very slight cooling and measurements were taken (Table IV) for a 12·5-ppm solution of tellurium.

TABLE IV.—FLUORESCENCE INTENSITIES FOR TELLURIUM

Wavelength, *Å*	Recorder reading	Relative line intensity (source)
2143	44	1
2383	60	2 5
2386		4
2259	2 5	10
2531	0	1 3

With analysing-monochromator slit-widths ranging from 0·5 to 2·00 mm, the 2383 and 2386 Å lines could not be resolved. The relative intensity readings were taken with a slit-width of *ca.* 0 005 mm.

The resonance line at 2143 Å was selected for further measurements because the flame background at this wavelength was much less than that at 2383 and 2386 Å. With a photomultiplier more sensitive in the ultraviolet, the 2143 Å line would probably give increased sensitivity.

Linear calibration curves were obtained with a slit-width of <2 0 mm over the concentration range 0 12–125 ppm of tellurium. Again, more concentrated solutions were not examined. The limit of detection was about 0 05 ppm and the limit of determination was 0·12 ppm.

Interferences

The effect of a 100-fold molar excess of the following selected range of cations was investigated on both selenium and tellurium: Ag, Al, Co(II), Cu(II), Fe(II), Hg(II), Mg, Na, NH_4, Pb, Sb(III) and Zn. In addition, the effect of a similar excess of selenium on tellurium and *vice versa* was examined. The results are summarized in Table V. All solutions were acidified with 2*M* nitric acid to prevent any precipitation. Sodium gave about a 20% increase in the fluorescence signal and this was found

TABLE V.—INTERFERENCE EFFECTS WITH ATOMIC-FLUORESCENCE SPECTROSCOPY

Element	Intensity of signal		Difference, %	
	Se	Te	Se	Te
—	75	75	—	—
Ag^{+}	76	79	+1	+4
Al^{3+}	79	76 5	+5	+2
Co^{2+}	76	72	+1	−4
Cu^{2+}	76 5	74	+2	−1
Fe^{2+}	75	75	0	0
Hg^{2+}	73 5	79	−2	+5
Mg^{2+}	78	77	+4	+3
Na^{+}	94	95	+20	+22
NH_4^{+}	75	75	0	0
Pb^{2+}	77	76 5	+3	+2
Se^{4+}	—	75	—	0
Sb^{3+}	74	75	−1	0
Te^{4+}	75	—	0	—
Zn^{2+}	75	73	0	−3

to be because of intense light emission from the flame and a slight light-leak in the monochromator. This increased signal was given at all wavelengths. All other elements produced signal differences of less than 5%.

Atomic-Absorption Measurements

The "absorption" mode of operation was now used and the electrodeless discharge tubes were placed in approximately the same position as hollow-cathode lamps would be in for absorption studies. The source was thus chopped at 100 c/s. A 7-cm long air–propane flame was used.

Selenium

The discharge tube was run at 30 W with moderate cooling and placed so that it was slightly out of focus at the entrance slit, in order to reduce the amount of light passing through the flame

The 1961 Å resonance line absorbed most strongly, the 2040 Å line absorbed about a fifth as much, and the 2063 Å line absorbed still less. The intercombination lines at 2075 and 2164 Å did not absorb at all. The limit of detection (for 1% absorbance) was 1 ppm, using the 1961 Å line. Linear calibration curves were obtained from 5–100 ppm of selenium. The range could be extended beyond this if desired.

Moderate cooling of the discharge tube was found to be essential as the absorbance decreased by a factor of about 3 if the tube was not cooled, and also the calibration graph curved towards the concentration axis. Over-cooling gave a very unstable tube and the discharge tended to be extinguished.

The absorption at the 1961 Å line was similar in air–propane and air–acetylene flames. Both of these flames absorbed *ca.* 70% of the radiation at 1961 Å. Atomic absorption occurs more strongly in air–acetylene than in air–propane flames because this line does not emanate from the ground state, but a state 0·25 eV above it.

Tellurium

The discharge tube was run at 20 W with very slight cooling and was arranged in the same way as the selenium discharge tube.

The 2143 Å resonance line absorbed most strongly and the 2383 and 2386 Å lines absorbed only about a tenth as much. The intercombination line at 2259 Å absorbed only slightly and the other intercombination line at 2531 Å did not absorb at all.

The limit of detection (for 1% absorbance) was 1 ppm with the 2143 Å line, and linear calibration curves were obtained over the range 5–100 ppm.

DISCUSSION

These studies show the advantages to be obtained by measuring the fluorescence emission instead of the absorption. Table VI compares the sensitivities of the two methods, with the same instrument and the same spectral sources for selenium and tellurium.

TABLE VI.—SENSITIVITIES FOR Se AND Te BY ATOMIC-FLUORESCENCE AND ATOMIC-ABSORPTION SPECTROSCOPY

	AFS		AAS	
	Se	Te	Se	Te
Limit of determination, *ppm*	0 25	0 12	5	5
Limit of detection, *ppm*	0 15	0 05	1	1

The sensitivities of these atomic-fluorescence methods are about 10 times greater than those of the atomic-absorption methods. Improvements in the detector response would have produced a still greater increase in sensitivity *e.g.*, a further factor of 10 is quite possible.

The examination of selected extraneous ions in the atomic-fluorescence studies also shows that the method is at least as free from inter-element effects as atomic-absorption spectroscopy.

The application of electrodeless discharge tubes as spectral sources means that the atomic-fluorescence method need not be restricted by the commercial availability of intense sources of excitation, a criticism once levelled at this technique. These sources, as well as fulfilling the essential requirements of high intensity and stability, possess the advantages of ease of manufacture and low cost. Also, from our somewhat limited experience, it would appear that they have a long "shelf-life". The selenium tube, for example, was not used for approximately 3 months, but it immediately gave the same output on operation as when last used. This also indicates the reproducibility of the source intensity. We have no reason to suspect that most other tubes should not behave in a similar manner. Such properties mean that electrodeless discharge tubes could also be used to advantage in atomic-absorption spectroscopy instead of hollow-cathode lamps, which are generally far from ideal.

As with hollow multi-cathode lamps, it should be similarly possible to obtain spectra of a number of different elements in the same tube. This has already been achieved in many instances because of impurities in the major compound or element, *e.g.*, iron in niobium, and mercury from the vacuum line. Because the spectral intensity is more dependent on the volatility of the element or compound than on its actual concentration, the impurity spectral lines in many instances may be as strong as those of the major constituent. Very intense continuous sources can also be made quickly and easily by introducing hydrogen, xenon, sulphur, iodine, *etc.* into the tubes. Electrodeless discharge tubes of these and other types should also find considerable application as spectral sources in solution spectrofluorimetry and other photo-techniques where intensity is one of the major requirements.

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Résumé—On dose le sélénium et le tellurium jusqu'à des concentrations aussi faibles que 0,25 et 0,12 ppm respectivement par mesure des signaux de fluorescence atomique à 2040 et 2143 Å respectivement. On considère en détail d'autres longueurs d'onde de mesure possibles et examine les effets de quelques ions étrangers. Comme sources spectrales on utilise des tubes à décharge sans électrodes excités par micro-ondes et les mesures d'intensité sont effectuées avec un spectrophotomètre d'absorption atomique/émission de flamme Unicam

SP 900A. On effectue aussi les mesures d'absorption atomique avec les mêmes sources et le même spectrophotomètre. On discute des avantages des méthodes de fluorescence atomique et de l'emploi des tubes à décharge sans électrodes.

Zusammenfassung—Selen und Tellur werden bis herunter zu 0,25 und 0,12 ppm durch Messung der Atomfluoreszenz-Signale bei 2040 Å bzw. 2143 Å bestimmt. Andere mogliche Meßwellenlängen werden im einzelnen erortert und der Einfluß einiger Fremdionen untersucht. Als Lichtquellen werden mit Mikrowellen erregte elektrodenlose Entladungsrohren verwendet. Die Intensitaten werden mit einem Unicam SP 900 A Atomabsorptions-/Flammenemissionsspektrophotometer gemessen. Messungen der Atomabsorption werden mit denselben Lichtquellen und demselben Spektrophotometer vorgenommen. Die Vorteile der Atomfluoreszenzmethoden und der Gebrauch elektrodenloser Entladungsrohren wird diskutiert.

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PHOTON-ACTIVATION ANALYSIS OF CAESIUM*

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Summary—The corrosive behaviour of caesium has been attributed in part to the presence of a non-metallic impurity such as oxygen. A photon-activation method for determining oxygen and carbon in caesium is described. Scintillation coincidence-counting and pulse-height discrimination are used to count the gamma-ray activity resulting from annihilation of the positrons emitted. Variation of beam energy has been investigated in order to obtain optimum irradiation conditions. In the samples analysed and under the conditions used, less than 100 ppm of oxygen and carbon can be detected. Results are compared with those from other methods.

THE development of high-temperature hydraulic fluids and thermionic propulsion systems has resulted in considerable investigations of alkali metals. The importance of this class of metals is attributed largely to their excellent properties as a heat transfer medium, a hydraulic fluid, and as a low ionization potential propellant.[1] However, their highly corrosive attack on most materials is a major deterrent to their use.

Experimental evidence, compiled within the last few years, indicates that the presence of impurities, even in trace amounts, often has a significant adverse effect on the properties of the alkali metals.[2] The corrosive behaviour of caesium, and of the other alkali metals, has been ascribed in part to the presence of oxygen as trace impurity. Current handling techniques are not sufficient to preclude occurrence of such impurities. In studies of methods of overcoming the corrosion problem, there is a need to correlate the effect of impurities in an alkali metal with the deterioration of the system. This report concerns the analytical technique for the determination of oxygen in caesium.

Most of the impurities commonly found in caesium are non-metallic, because of its extreme reactivity with air. In addition to the Kjeldahl method for nitrogen determination, chemical methods have been developed for the determination of non-metallic impurities in alkali metals. In the past, the amalgamation,[3] Wurtz reaction[4] and gas fusion methods[5] have been the principal techniques used for oxygen in alkali metals. Combustion methods for carbon determination have also been

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used. All of these methods require the complete quantitative removal and recovery of the impurities, as otherwise serious errors may occur.

Recently, the more attractive radioactivation methods have been examined. These are non-destructive and do not require removal of the element. In the fast neutron reaction, neutrons produced by a generator or accelerator are used to bombard the sample. Nitrogen-16 is produced. Measurement of the 7-sec half-life nitrogen-16 requires the immediate analyis of the sample after irradiation. A rapid transfer system is mandatory for trace amounts of oxygen. Normally only one element can be determined at a time, and large sample sizes are sometimes required. Reactions induced by helium-3 have also proved popular.[6] This method is quite promising, but the limit of penetration of the helium beam confines use of this method essentially to surface studies.

Because of the disadvantages mentioned above, photon activation analysis was investigated for the analysis of caesium. Although oxygen was the impurity of interest the possibility of determining carbon and nitrogen was also examined.

Photon activation

The determination of oxygen, nitrogen and carbon by radioactivation, with photons produced by a betatron, was shown to be possible by Basile, Hure, Leveque and Schuhl in 1954.[7] Beard, Johnson and Bradshaw[8] have claimed that less than 10 ppm of oxygen can be detected in beryllium. Englemann[9] has also demonstrated the feasibility of this technique in the analysis of beryllium, calcium and boron.

Interaction of a bremsstrahlung beam of a betatron with matter may produce radioactivity through the following reaction (γ, n), (γ, p), (γ, np), $(\gamma, 2n)$, *etc.* In addition, certain elements can undergo (γ, γ') reactions and produce nuclear isomers through isomeric transition.[10] The principal reaction depends upon the target material and photon energy. For oxygen, carbon and nitrogen, and a photon energy between 20 and 30 MeV, the (γ, n) reaction is predominant. The isotopes produced by this reaction, especially for elements of low atomic number are generally positron emitters which produce annihilation radiation.

The photon-activation method was used in our analysis of caesium. The impurity of interest is mainly oxygen; however, carbon was also detected. Nitrogen was not found. This was probably due to the lack of reactivity of caesium with nitrogen under ordinary conditions.

The radioisotopes produced by the (γ, n) reaction of oxygen and carbon are oxygen-15 and carbon-11. Both are positron emitters.

EXPERIMENTAL

Chemicals

Oxygen standard. Distilled water was used as the standard for oxygen.

Caesium. The extreme reactivity of caesium with the atmosphere made it necessary to load the samples in a vacuum dry box under an atmosphere of purified helium. In addition, unique handling techniques were developed for transferring the caesium, after irradiation, to another container for counting with little loss in time and without the reactive metal igniting. Some samples were deliberately contaminated before loading in order to provide a range of concentration of impurity.

Apparatus

Radiation. The samples were irradiated at between 20 and 30 MeV in the X-ray beam of a Brown-Boveri betatron located at Montefiore Hospital, Bronx, New York. The samples and standards were bombarded in the same positions for equivalent times. A holder was fabricated to ensure

identical geometrical position each time. About 1 min was taken to place the sample in the counter.

Counting. Scintillation coincidence-counting and pulse-height discrimination were used in counting the γ-ray activity resulting from the annihilation reaction of the positrons. Two thallium-activated sodium iodide crystals, 2 in. in diameter and 3 in. long, were used to detect the 0·51 MeV annihilation photons. The crystals were mounted on photomultipliers, the pulses from which were amplified; the output from a transistorized dual pulse-height analyser was fed into a coincidence discriminator with a 1-μsec resolving time. A transistorized high-speed scaler recorded the output. The windows of the pulse-height analyser were adjusted for 0·51 MeV energy, sodium-22 being used as a calibration source.

Procedure

The glass ampoules were quickly broken after irradiation and the caesium transferred with a syringe under a protective layer of paraffin oil to a polyethylene container for counting. The paraffin oil was necessary in order to prevent the caesium from igniting in air. The transfer of caesium eliminated container blanks which are normally found in oxygen analysis. The entire operation of removing the caesium and placing it in the counter took about 1 min. The exact amount of caesium transferred was obtained by weighing the polyethylene containers after counting.

The irradiation time and beam energy selected depend on the host material and the impurities present. Since our principal interest in caesium is detecting oxygen, fairly short irradiation times were used.

Irradiation at about 25 MeV exceeds the threshold for (γ, n) and (γ, γ') reactions. The short

TABLE I.—IMPURITIES DETECTED IN CAESIUM BY EMISSION SPECTROGRAPHIC ANALYSIS

Impurity	Average concentration, % w/w
Fe	0·0005
Cr	0·0015
Mg	0 0020
Al	0 0010
Pb	0 0010
Ni	0·0025
Ca	0 0015
Sn	0 0025
K	0·0005
Rb	0 0020
Na	0·0050
Cu	0·0010

irradiations will not induce contribution of long-lived isotopes to the total activity. Likewise isotopes with very short half-lives will decay almost completely before counting is started. The only isotopes to be considered are those whose half-lives fall within the time interval of interest.

All of the radioactivity produced is assumed to be the result of the contribution of each isotope. Since oxygen is the major impurity of interest, irradiations of 2–8 min were used. The short half-life of oxygen-15 (2·1 min) makes it resolvable from the other isotopes present. The concentration of metallic impurities found in typical samples by emission spectroscopy is shown in Table I. In addition to the detected impurities, silicon and chlorine are also assumed to be present.

RESULTS AND DISCUSSION

Sensitivity

The counting rate to be expected from a known amount of oxygen in an irradiated sample can be computed. If we assume a 5 mbarn (γ, n) cross-section[11] for oxygen at 35 MeV at a photon flux of 10^9 photons/cm^2/sec, we can calculate the expected activity from the equation

$$A = \frac{M}{N}\theta\phi\sigma(1 - e^{-\lambda_0 t}) \qquad (1)$$

where

A = disintegrations/sec/g of oxygen
N = Avogadro's number
M = atomic weight of oxygen = 16
σ = (γ, n) cross-section for oxygen at 35 MeV = 5×10^{-27} cm^2
θ = isotopic abundance of ^{16}O
ϕ = photon flux at 35 MeV gamma-energy = 10^9 photons/cm^2/sec
λ_0 = decay constant for ^{15}O = 0·330
t = irradiation time (assume saturation or infinite irradiation).

Substitution in equation (1) gives $A = 1{\cdot}2 \times 10^7$ disintegrations/min/g of oxygen. Assuming 30% efficiency for the counting equipment, $A = 3{\cdot}6 \times 10^6$ cpm. In one experiment, 1 g of oxygen in the form of water gave $1{\cdot}4 \times 10^6$ cpm. These calculations are only used to compare theoretically expected counts with the experimental activity observed in our work. In practice, counting rates of unknowns were run against standards for precise results. However, this calculation indicates that theoretically it is possible to determine oxygen below 10 ppm if no interfering reactions occur.

Optimum conditions

In order to determine the optimum irradiation conditions to be used, a series of experiments was carried out. Duplicate samples of caesium loaded at the same time were irradiated for 2 min at beam energies ranging from 25 to 35 MeV. Counting times were the same for all samples. One-gram quantities of water were also irradiated under the same conditions as the caesium. A plot of activity *vs.* energy is shown in Fig. 1.

It can be seen from the plot, that from 25 MeV to about 27 MeV the induced radioactivity in the caesium samples increases proportionally. However, at approximately 28 MeV and above, the activity increases much more than expected. Possibly, some other reactions are occurring such as (γ, 2n) (γn, p), *etc.* In the water sample the induced activity increased steadily with irradiation energy up to 27 MeV. Above 27 MeV the rate of increase in activity was less. Consequently it was decided to irradiate with energies below 28 MeV in order to decrease the amount of induced extraneous activity.

Analysis of caesium

Two methods of analysing the results were used—algebraic and graphical.

Mathematical. Samples of caesium were prepared and irradiated in the betatron at 25 MeV. The counting rate observed at any time after the conclusion of the irradiation can be expressed as

$$A(t) = A_0 e^{-\lambda_c t} + A_c e^{-\lambda_c t} \tag{2}$$

where

λ_0 = decay constant for oxygen
λ_c = decay constant for carbon
$A(t)$ = measured activity at time t
A_0 = activity of oxygen at time = 0
A_c = activity of carbon at time = 0.

All of the activity is assumed to be contributed by oxygen and carbon only, since nitrogen was not detected. Chemical analysis of caesium for nitrogen also failed to detect any appreciable quantity of nitrogen. With the irradiation times employed and concentration present, nitrogen would not contribute any measurable activity and hence its contribution was neglected. The contribution of other metallic impurities is small, due to the concentration present, the half-lives and the abundance, as seen in Table II.

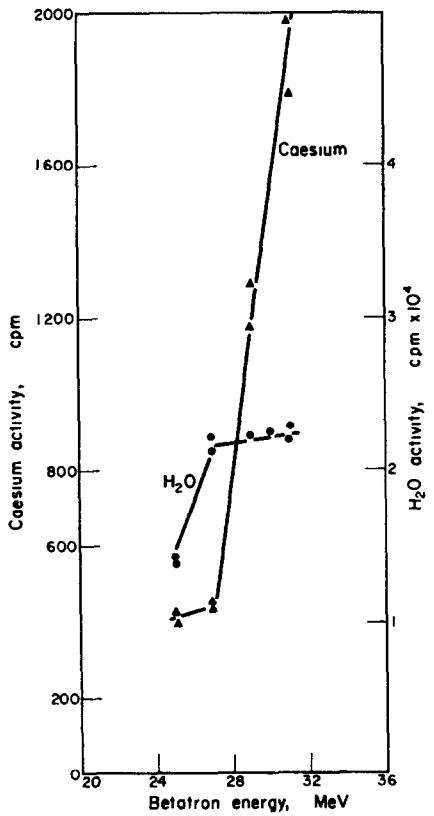

FIG. 1.—Activity *vs.* betatron energy.

By choosing two sufficiently separated observation times, two useful simultaneous equations are obtained. Since oxygen-15 and carbon-11 are detected in the samples, 2 min and 20 min are taken as the time intervals. The decay constants for oxygen-15 and carbon-11 are 0·330 and 0·0338 min^{-1} respectively.

For example, a sample of caesium weighing 2·103 g was prepared and irradiated at 25 MeV in the betatron. The activity at 2 min and 20 min is substituted in equations (2); solution of the resulting equations gives the coefficients $A_0 = 14$ cpm and $A_c = 28$ cpm. These coefficients represent the activity of each component at zero time. The total activity in cpm is then obtained by substituting A_0 and A_c in equation (2). The plot of this expression is shown in Fig. 2 as a solid line. The contributions of oxygen and carbon are shown as broken line curves.

One sample of distilled water weighing 1·034 g was used as the standard for oxygen. It was irradiated for 2 min under geometrical conditions identical with those

TABLE II.—PROPERTIES OF IMPURITIES IN CAESIUM UNDERGOING REACTIONS WITH PHOTONS*

Stable isotope	Abundance, %	Positron-emitting isotope	Half-life
^{16}O	99 76	^{15}O	2 1 min
^{12}C	98 89	^{11}C	20 5 min
^{14}N	99 63	^{13}N	10·0 min
^{23}Na	100	^{22}Na	2·6 yr
^{39}K	93 2	^{38}K	7 7 min
^{85}Rb	72·2	^{84}Rb	33 day
^{40}Ca	96·9	^{39}Ca	1 0 sec
^{54}Fe	5 9	^{53}Fe	9 min
^{63}Cu	70 1	^{62}Cu	10 0 min
^{65}Cu	29·9	^{64}Cu	12 8 hr
^{58}Ni	68·0	^{57}Ni	36 hr
^{27}Al	100	^{26}Al	6 5 sec, 10^6 yr
^{24}Mg	78 8	^{23}Mg	12 sec
^{28}Si	92·17	^{27}Si	4·4 sec
^{50}Cr	4 4	^{49}Cr	42 min
^{35}Cl	75·53	^{34}Cl	32 4 min
^{117}Sn†	7 6	^{117}Sn	14 day
^{119}Sn†	8·6	^{119}Sn	250 day
^{204}Pb†	1 3	^{204m}Pb	68 min

* (γ, n) unless otherwise noted.
† (γ, γ'), metastable isotope does not emit positrons.

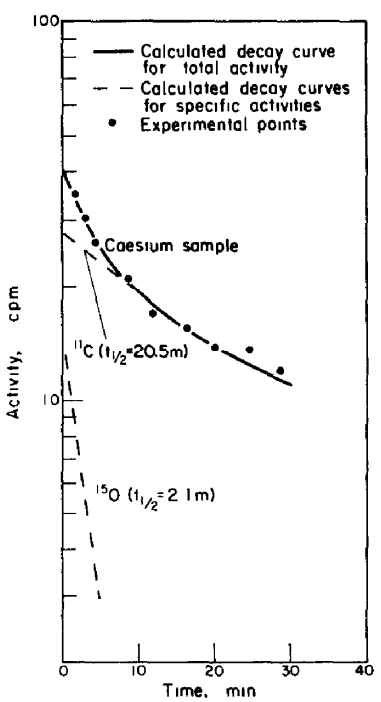

FIG. 2.—Decay of activities in caesium after photon irradiation for 8 min

used for the caesium. The count-rate for an infinite irradiation was 7×10^4 cpm. The oxygen concentration in the unknown sample of caesium was found by normalizing for differences in weight, density and bombarding intensity between the standard and the unknown. The amount of oxygen found was 0·0058%.

A similar procedure was used for carbon. A 1-g sample of polyethylene was irradiated under the same conditions for 2 min. The amount of carbon found was 0·0019%.

Graphical. A graphical method was also used for resolving some of the composite decay curves. Results obtained were in agreement with those obtained algebraically.

Accuracy. Because of the difficulty in adding precise amounts of oxygen to caesium, a chemical method[12] using a liquid ammonia extraction apparatus was used as a check. Duplicate samples of caesium were loaded at the same time in the dry box and analysis by both methods was carried out. Results are shown in Table III.

TABLE III.—COMPARISON OF ACTIVATION AND CHEMICAL METHODS

Caesium sample	Carbon	Oxygen		Beam energy, *MeV*
	Photon activation, *ppm*	Photon activation, *ppm*	Chemical method, *ppm*	
1D	342	1142	1180	35
7M	75	247	224	35
8M	150	497	469	35
9D	80	258	273	35
10M	33	118	98	25
11D	15	57	41	25
12D	19	58	50	25
13M	—	117	94	25
14D	—	27	18	25
15M	—	20	24	25
16M	—	17	22	25

Some samples were deliberately contaminated in order to give a range of oxygen and carbon values.

Samples of caesium were analysed for oxygen at the request of the U.S. Air Force. Two types of samples were submitted. The Air Force designated these samples as "high" and "low" oxygen. The results are shown in Table IV together with those from other laboratories.

TABLE IV.—ANALYSIS OF AIR FORCE SAMPLES

	Oxygen, *ppm*	
	"Low"	"High"
Republic	25 ± 6*	55 ± 8*
Lab A	11 ± 5	56 ± 5
Lab B	10 ± 5	96 ± 5

* Sample weights were 2·0–2·4 g.

DISCUSSION

Photon activation analysis appears promising for the determination of trace impurities in suitable materials. Oxygen determination in caesium was emphasized at

the time because of the discrepancies that existed in the various analytical methods. Carbon was detected in the samples analysed, but nitrogen was not found. The detection of oxygen and carbon is probably due to the extreme reactivity of caesium with oxygen, carbon dioxide and water vapour in the air.

The decision to classify nitrogen as an undetectable trace contaminant was made after considerable evaluation. Nitrogen does not react with caesium under normal conditions, and hence if it is present it is in very low concentrations.[13] The supplier of caesium claims that less than 5 ppm of nitrogen is present. A modified Kjeldahl method of analysis was performed and less than 3 ppm of nitrogen was found. Computer analysis also indicated the absence of any contribution of nitrogen activity to the total activity measured after activation.

The nitrogen activity expected can be estimated from the concentration found by chemical analysis and the estimated cross-section reported by Johns, Horsley, Haslam, and Quinton.[14]

The (γ, n) cross-section for nitrogen is approximately one-third that of oxygen and carbon—about 1·7 mbarn at 35 MeV. The activity expected for 1 g of nitrogen at 25% saturation, calculated from equation (1), is $5{\cdot}4 \times 10^5$ cpm. For 1 μg of nitrogen, the activity contributed is negligible.

In the present work, some interfering activity was encountered for low levels of oxygen when irradiation energies above 28 MeV were used. It appears that this interfering activity is due to some reaction other than (γ, n). Irradiations at 35 MeV were initially used for determinations at higher levels of oxygen, with no interference. However, when lower levels of oxygen were determined, the background activity was sufficient to cause interference. The results in Table IV shows irradiations performed at both 25 and 35 MeV. For low oxygen values, irradiations below 28 MeV were used; but lowering the beam energy also decreases the photon flux, and hence reduces the activity. Deviation from the calculated decay curve occurs after 20 min. This is probably due to other impurities present and to the large statistical variation arising from the low number of counts. Even with the reduced flux, less than 100 ppm of oxygen and carbon in caesium have been determined.

Under the experimental conditions used, the accuracy of the method for low levels of oxygen is estimated to be $\pm 25\%$ with a precision of about 10%. These values are based upon the experimental variables and agreement of results found for the experiments performed. Results for oxygen compare favourably with a chemical method and with those of several other laboratories.

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Zusammenfassung—Das korrosive Verhalten von Caesium wurde zum Teil einer nicht metallischen Verunreinigung wie Sauerstoff zugeschrieben. Eine Photonenaktivierungsmethode zur Bestimmung von Sauerstoff und Kohlenstoff in Caesium wird beschrieben. Mit Szintillations-Koinzidenzzählung und Impulshöhendiskriminierung wird die aus der Zerstrahlung der emittierten Positronen herruhrende Gamma-Aktivität gezahlt. Um die besten Bestrahlungsbedingungen zuerhalten, wurde die Veranderung der Bestrahlungsenergie untersucht. Unter den verwendeten Bedingungen lassen sich in den untersuchten Proben weniger als 100 ppm Sauerstoff und Kohlenstoff nachweisen. Die Ergebnisse werden mit denen anderer Methoden vergleichen.

Résumé—On attribué pour partie le comportement corrosif du caesium à la présence d'une impureté non métallique comme l'oxygène. On décrit une méthode par activation de photons pour le dosage de l'oxygène et du carbone dans le caesium. On utilise les comptages par scintillation en coïncidence et d'impulsion avec discrimination pour compter l'activité des rayons gamma résultant de la destruction des positrons émis. On a étudié la variation de l'énergie du faisceau afin d'obtenir les conditions d'irradiation optimales. Dans les échantillons analysés, et avec les conditions utilisées, on peut détecter moins de 100 ppm d'oxygène et de carbone. On compare les résultats à ceux d'autres méthodes.

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RAPID MICROCHEMICAL METHOD FOR THE DETERMINATION OF MAGNESIUM IN BIOLOGICAL FLUIDS

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Summary—A photometric method for the determination of magnesium in the presence of up to 50-fold excess of calcium is described. A magnesium–Azovan Blue lake is formed, stabilized with polyvinyl alcohol, and the absorbance is measured (Kodak No. 7 filter). The method has been used to determine magnesium in sera.

MUCH significance has recently been attached to the study of magnesium metabolism in living organisms. The two major spectrophotometric methods for the determination of magnesium are (*a*) the Titan Yellow method[1] and (*b*) the Eriochrome Black T method.[2] The first of these dyes forms a pink lake and the other a true complex with magnesium in alkaline medium. Both are subject to interference by calcium in the determination of magnesium in biological fluids.[3–8] The separation of calcium by precipitation leads to negative errors because of co-precipitation and adsorption of magnesium.[9,10]

A new colorimetric method free from interference by other alkaline earth ions is desirable. The method described here, based on Evans (Azovan) Blue, is shown to be satisfactory for the determination of magnesium in biological fluids.

EXPERIMENTAL

Reagents

Sulphuric acid, 0·33*M*.

Sodium tungstate solution, 10% w/v.

Titan Yellow solution, 0·05% w/v. Place in an amber bottle and store in a refrigerator. The solution is stable for a week.

Azovan Blue 0·04% w/v. A B.D.H. (laboratory reagent grade) sample was used. This solution is stable at room temperature for at least a month. This solution may have to be diluted if a spectrophotometer is used instead of an absorptiometer.

Polyvinyl alcohol (PVA). Dissolve 50 mg of PVA in 50 ml of water by warming to 65° with constant stirring. Dilute the solution to 100 ml, filter, and store in a refrigerator.

Polyethylene glycol solution, 0·1%.

Polypropylene glycol solution, 0·1%.

Methyl cellulose solution, 0·05%. Prepare in the same way as the solution of PVA.

Standard magnesium solution, 0·5 g/l. Dissolve 0·5125 g of magnesium sulphate heptahydrate in water and dilute to 100 ml. Dilute this stock solution to give a working standard solution containing 10 μg of magnesium per ml.

Sodium hydroxide solution, 4*M*.

All the reagents were obtained either from Merck or B.D.H. and except where stated were of analytical reagent grade. Distilled water was used throughout.

Apparatus

A Spekker absorptiometer was used for colorimetric measurements

Standard curves for magnesium with Titan Yellow and Azovan Blue

Place 5 portions of working standard solution containing 2–10 μg of magnesium in test-tubes and dilute each to 3 ml. Add 1 ml of the sodium tungstate solution and 1 ml of 0·33*M* sulphuric acid to each tube. Mix the contents thoroughly and transfer 2–5 ml portions from each tube to another set of 5 test-tubes. Add 1 ml of polyvinyl alcohol solution and 0·5 ml of dye solution to all the tubes and mix the contents. Slowly add down the side of the tube 1·0 ml of 4*M* sodium hydroxide and mix gently. Five minutes after addition of the alkali measure the absorbance in a 1-cm cell against a blank solution. Use Kodak filters Nos. 5 (550 mμ) and 7 (610 mμ) for Titan Yellow and Azovan Blue respectively. The Azovan Blue colour is quite stable for up to 6 hr. Standard curves for magnesium with both dyes are shown in Fig. 1.

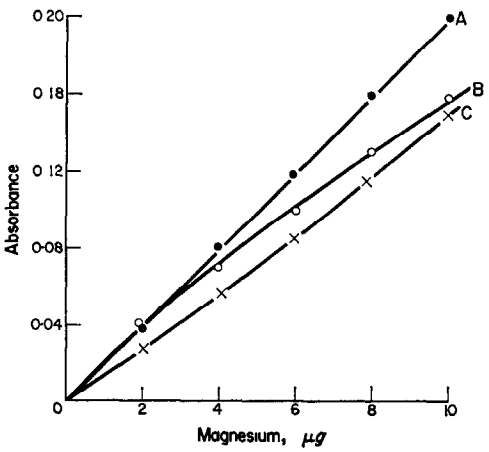

FIG. 1.—Standard curves for determination of magnesium with Azovan Blue and Titan Yellow.

A—Azovan Blue, Kodak Filter No. 7
B—Azovan Blue, Kodak Filter No. 8
C—Titan Yellow

Procedure for the determination of magnesium in serum and spinal fluid

Separate serum from the clot as soon as possible to avoid the migration of magnesium from red blood corpuscles to the serum. Place 0·5 ml of serum or spinal fluid in a test-tube, and dilute it to 3 ml with distilled water. Add 1 ml of sodium tungstate solution and 1 ml of 0·33*M* sulphuric acid. Mix well and then centrifuge. Take 2·5 ml of the supernatant fluid and complete the colour development in the way described above. Develop an aqueous standard for each batch of sera.

RESULTS AND DISCUSSION

Recovery was tested by the addition of known amounts of magnesium to the serum, and found to be at least 85%.

Gum-ghatti, polyvinyl alcohol (PVA), polyethylene glycol (PEG), polypropylene glycol and methylcellulose in the concentration range 0·05–1% were examined as potential stabilizers of the magnesium lake. PVA, methylcellulose and PEG stabilized the lake for more than an hour, but in the present investigation 0·05% PVA solution was used.

The lake forms only at high pH. To determine the optimum conditions, the colour was developed at different concentrations of alkali (Table I). The concentration of sodium hydroxide between 2 and 10*M* does not affect the sensitivity. However, 4*M* sodium hydroxide was found to be most suitable because at higher concentrations of alkali bubbles form in the solution and the viscosity increases, and at lower concentrations the results are not reproducible. The absorbance of the lake was measured

TABLE I.—ABSORBANCE OF Mg-DYE LAKE IN PRESENCE OF VARIOUS CONCENTRATIONS OF ALKALI SOLUTIONS

NaOH, *M*	Drum reading	
	5 μg Mg	10 μg Mg
2	0·10	0 17
4	0 105	0·185
6	0·10	0·23
8	0·115	0·23
10	0 11	0 22

against a blank with different filters. Beer's law is obeyed and the greatest absorbance is obtained when a Kodak filter No. 7 is used.

To determine the amount of dye required per μg of magnesium, dye solutions of different concentrations were used. The results are shown in Fig. 2, from which it is

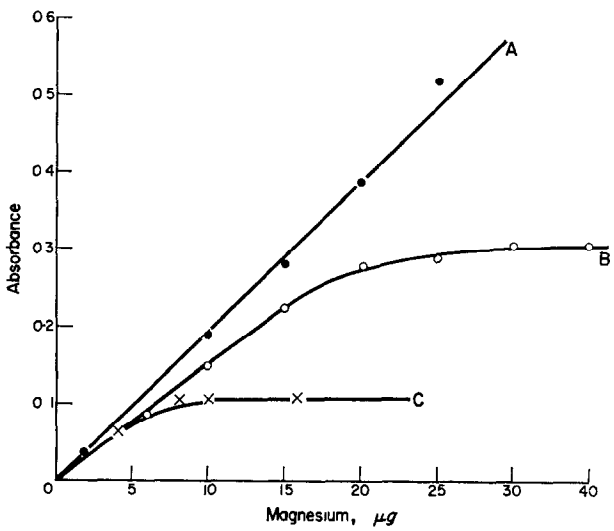

FIG. 2.—Standard curves for determination of magnesium with varying concentrations of Azovan Blue.
A—Azovan Blue 40 mg/ml
B—Azovan Blue 20 mg/ml
C—Azovan Blue 10 mg/ml

concluded that about 6·7 μg of dye per μg of magnesium is the optimum ratio and that the mole ratio of magnesium to dye in the lake is 6:1. The molar absorptivity is $2{\cdot}4 \times 10^3$ cm^2. mmole^{-1}. The sensitivity with Azovan Blue is greater than that with Titan Yellow.

Most biological materials contain a variety of cations of which only calcium may be expected to interfere under the conditions of the reaction. Magnesium and calcium react with many azo dyes in alkaline medium through either two *o,o'*-hydroxyl groups or one *o*-hydroxyl and one *o*-carboxyl group.[11] The advantageous feature of this dye is that it is less subject to calcium interference than other azo dyes which have been proposed for the determination of magnesium (Table II).

A calcium/magnesium ratio of 50 does not affect the determination of magnesium by the Azovan Blue method, but a ratio of 10 is the maximum tolerable in the Titan Yellow method.

TABLE II —ABSORBANCE OF Mg-DYE LAKE IN PRESENCE OF CONSTANT AMOUNT OF MAGNESIUM AND DIFFERENT AMOUNTS OF CALCIUM

Magnesium, μg	Calcium, μg	Drum reading	
		Azovan Blue	Titan Yellow
10	0	0 20	0 17
10	25	0 195	0 175
10	50	0 198	0 17
10	100	0 20	0 175
10	250	0 205	0 29
10	500	0 20	0 36

TABLE III.—DETERMINATION OF MAGNESIUM IN 100-ml SERUM SAMPLES BY THE TITAN YELLOW AND AZOVAN BLUE METHODS

Magnesium found, *mg* %		
Azovan Blue	Titan Yellow	Difference, %
2 42	2 32	+4
2 40	2 40	—
1 76	1·76	—
2 02	2 02	—
1 06	1 06	—
2 17	2 22	−2
2 19	2 22	−1
2 00	1 96	+2
1·85	1 96	−5
2 30	2 12	+7

Magnesium in 10 serum samples was determined by both methods (Table III). The results are in good agreement with each other. In cerebrospinal fluid samples, the magnesium content was found to vary from 1·0 to 3·4 mg/100 ml. It has been reported that the Titan Yellow method, used here for comparison, yields results on serum 10–15% higher than those obtained by the magnesium ammonium phosphate method.[12] It has been pointed out[4,13,14] that the presence of calcium intensifies the colour of the magnesium Titan Yellow lake, although it has been claimed[15–20] that calcium in the concentrations found in serum does not interfere. The results in Table II show that the colour of the Titan Yellow is only increased if the calcium concentration is ten times that of the magnesium. Thus, calcium would not be expected to interfere in the determination of magnesium in serum.

Acknowledgement—The authors are indebted to Dr. T. A. Venkatasubramanium, Department of Biochemistry, Patel Chest Institute and Dr. B. C. Ray Sarkar, Institute of Nuclear Medicine and Allied Sciences, for their keen interest and encouragement. The thanks of the authors are also due to Lt. Col. S. K. Mazumdar, Officer-in-Charge, Institute of Nuclear Medicine and Allied Sciences, for providing facilities.

Résumé—On décrit une méthode photométrique pour le dosage du magnésium en présence d'une quantité jusqu'à 50 fois supérieure de calcium. Il se forme une laque magnésium—Bleu Azovan, stabilisée à l'alcool polyvinylique, et l'on mesure l'absorption (filtre Kodak no 7). On a utilisé la méthode pour doser le magnésium dans les sérums.

Zusammenfassung—Ein photometrisches Verfahren zur Bestimmung von Magnesium neben bis zu 50-fachem Überschuß an Calcium wird beschrieben. Es wird ein Farblack aus Magnesium und Azovanblau gebildet, mit Polyvinylalkohol stabilisiert und die Extinktion gemessen (Kodak-Filter Nr. 7). Die Methode wurde auf die Bestimmung von Magnesium in Seren angewandt.

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APPLICABILITY OF THE QUASI-ADIABATIC ENTHALPIMETRIC METHOD FOR THE STUDY OF CHEMICAL KINETICS

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Summary—The thermal quasi-adiabatic method and the non-adiabatic one are compared for the study of chemical kinetics. With thermistors as temperature-sensitive elements, and a very simple apparatus, moderately fast reactions (with $t_{1/2}$ down to 2 sec) and consecutive reactions can be followed, and mixtures analysed with good accuracy. The reproducibility is satisfactory over a wide range of experimental conditions. The calculation of the kinetic parameters, for both first- and second-order kinetics is very simple and requires no calibration of the system. Application of the technique to the study of the alkaline hydrolysis of some alkyl acetates is described.

THE analysis of a mixture of two constituents with similar chemical properties is often difficult by traditional chemical or physical methods, but is easily achieved kinetically if the compounds react at sufficiently different rates with the same reagent. This method of analysis has been so greatly developed in recent years, especially for mixtures of organic compounds,[1–3] as to suggest the utility of setting up a kinetic technique which offers the advantages of (*a*) permitting use of different solvents without the loss of accuracy, (*b*) extensive application to many important chemical reactions in a rate-range often difficult to deal with, (*c*) rapidity, and (*d*) inexpensive and simple instrumentation, mostly readily available in the laboratory. The enthalpimetric method, in which the temperature changes of a system during a reaction under quasi-adiabatic conditions are measured with thermistors is particularly useful, and permits the rate constants of relatively fast reactions to be measured with a precision of $\pm 1\%$, and an accuracy presumably of the same order. This paper describes the conditions and limits of applicability of the method both in chemical kinetics and analytical chemistry.

The study of chemical kinetics through enthalpimetry has been pursued by various authors, principally with non-adiabatic conditions, using either a single reaction cell[4–9] or two cells for differential measurements.[10,11] Under these experimental conditions, by appropriately modifying the characteristics of the cell–thermostat separator one can follow relatively slow reactions[9] as well as relatively fast ones with $t_{1/2}$ down to 0·2 sec.[7]* The corresponding time–temperature curves are similar to those of two consecutive reactions and have a maximum, the quantity of heat playing the part of the intermediate compound. For first-order reactions, fairly good values of rate constants can be obtained from the values of time[4,6] or temperature[6–8] corresponding to the maximum. In the other cases different points in the ΔT *vs.* t curves must be used,[4,5,9–11] with a complicated and lengthy calculation.

* With the flow method, thermocouples being used to measure the temperature, very fast kinetics have been followed.[12]

Because of the method of calculus used in these methods, it is necessary to measure the ΔT value for the same reaction in adiabatic conditions, the exact relationship between temperature and the electrical quantity measured, and also the heat contribution due to the mixing of the reagents and the Newton heat–exchange constant.

It must finally be emphasized that the sign and magnitude of the heat of mixing, and the time lag corresponding to the mixing, greatly affect the accuracy of the results, limiting the applicability of the enthalpimetric method. At any rate, it cannot be usefully employed for the kinetic analysis of a mixture. The authors cited claim a precision of 5–10%, though for slow reactions (observation times of about an hour), Becker obtained a precision of 2–3%.[9] Recently, Walisch and Becker[14] have devised an experimental technique based on the use of the Peltier battery; they follow the kinetics of an exothermic reaction at a strictly constant temperature through control of the energy required by the Peltier battery to compensate for the heat of the reaction.

Wyatt[13] has described a method which is essentially adiabatic; the loss of heat from the reaction vessel to the environment was balanced, before and during the reaction, by means of a small heater. In our work, since the initial difference of temperature between the cell and the thermostatic bath was kept essentially zero, there was no need to compensate for heat loss and the use of thermistors instead of thermocouples simplified the instrumentation.

Calculation of the kinetic data for quasi-adiabatic conditions

The kinetic constant can be calculated graphically through a plot of V *vs.* t, where V is the signal of the unbalanced bridge containing the thermistor in one arm, and is proportional within certain limits[15] to ΔT.

Figure 1 shows an example of the curve recorded for a first-order reaction. In this, the line b—drawn tangentially to the experimental curve for times corresponding practically to 100% reaction—is parallel to the curve a recorded before the addition of the reactant (the slope of a depends on the mechanical agitation), and the distance d represents the heat of dilution.

The distances h of the points of the experimental curve c from the straight line b are proportional to the amount of unreacted substance $(a–x)$. The value of k is obtained directly from the slope of a plot of log h *vs.* t (curve e). The intercept for $t = 0$ allows computation of the value of h^0 in the case in which the experimental curve does not allow easy measurement of the contribution due to the heat of mixing (chemical reaction rate fast compared to mixing rate). The value of ΔH of reaction can be obtained from the value of h^0 by calibration of the system. Second-order kinetics can be treated in the same way. In this case the $(a–x)$ value is given by the corresponding value of $\left(\frac{(h^0 - h}{h^0}\right)a$; h^0 is generally obtained directly from the experimental V *vs.* t curve. When this cannot be done (because there is not a clear distinction between the heat of mixing and the heat of reaction) the heat of mixing is measured in a separate test. The activation energy can be obtained from a plot of log k against $1/T$ where T is the absolute temperature.

Analysis of a mixture

The law governing the reaction of a mixture of two compounds A and B simultaneously reacting with the same reagent with first-order kinetics is obtained by

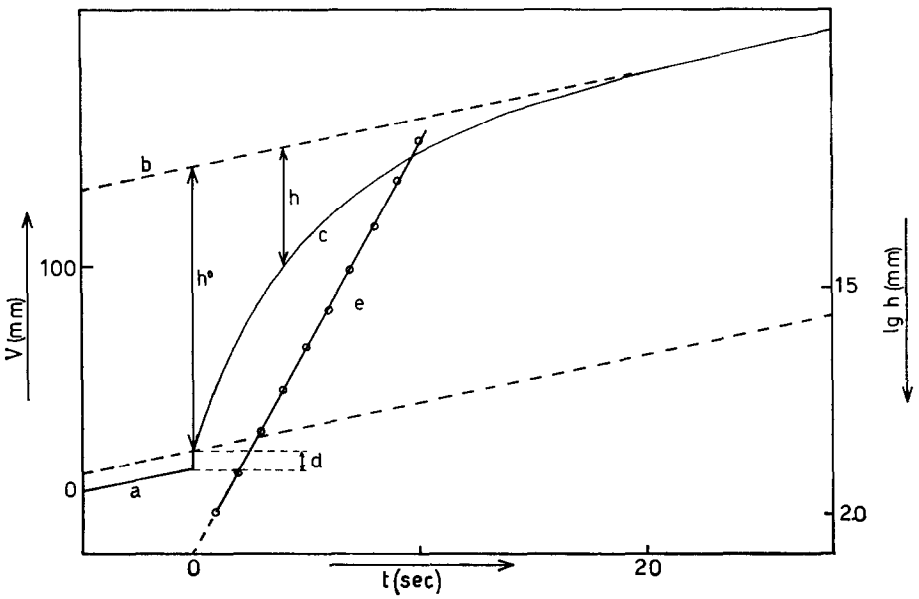


FIG. 1.—Example of quasi-adiabatic curve recorded during the hydrolysis of 0·012*M* methyl acetate with 0·50*M* NaOH at 32°C.
The intercept of log *h* (curve *e*) at $t = 0$ gives a value of $h^0 = 122$ mm; the value calculated directly from curve *c* is 125 mm. The curves are identified in the text.

combining the relationship valid for each of the individual components. Using the symbols from Fig. 1:

$$h_A = h_A^0 \,.\, \exp(-k_A t)$$

$$h_B = h_B^0 \,.\, \exp(k_B t).$$

Then

$$h = h_A + h_B = h_A^0 \,.\, \exp(-k_A t) + h_B^0 \,.\, \exp(-k_B t). \qquad (1)$$

The experimental curve *V vs. t* or ΔT *vs. t* which is obtained is of the type shown in Fig. 2. If the values of k_A and k_B are different enough, a plot of log *h vs. t* gives a curve of the type *a* in Fig. 2, from which it is possible to calculate the amount of A and B in the mixture. From curve *a* the value of log h_B^0 can be extrapolated when [A] has become negligible with respect to [B]. Under these conditions, equation (1) is reduced to:

$$\log h = \log h_B^0 - 2{\cdot}3 \,.\, k_B t. \qquad (2)$$

Once h_B^0 is known, the value of h_A^0 can be obtained from h^0 on the experimental curve. When this cannot be done, one can obtain h_A^0 by plotting log $(h - h_B)$ *vs. t* and extrapolating to $t = 0$ (curve *c* of Fig. 2).

The composition of the mixture can be obtained from the values of h_A^0 and h_B^0 by using either the values of ΔH and that of the calorimetric constant or an experimental relation between *h* and *c*.

A very quick method for finding the values of h_A^0 and h_B^0 is that of using only one point of the experimental curve in addition to the value of h^0.[3]

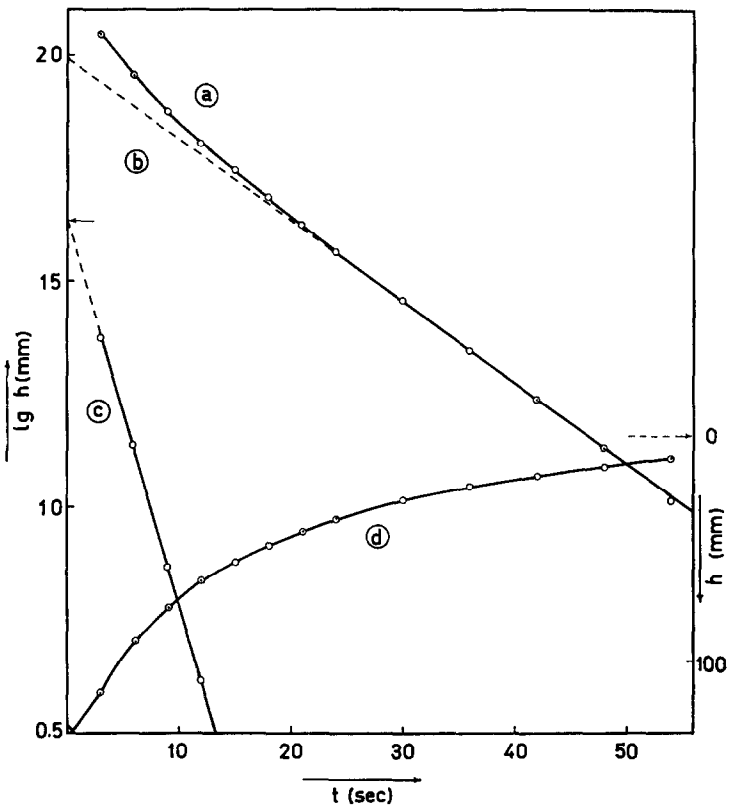


FIG. 2.—Kinetic analysis of a mixture of methyl acetate (0·424 mmole) and isopropyl acetate (0·848 mmole).
(*a*) Log h [$= \log(h_{Me} + h_{isoPr})$] *vs.* t.
(*b*) Extrapolation of curve (a) to give h^0_{isoPr} as the intercept, corresponding to $h_{Me} \ll h_{isoPr}$.
(*c*) Log $(h - h_{isoPr})$ *vs.* t. The intercept gives the value of h^0_{Me}.
(*d*) Experimental values for h *vs.* t.

From equation (1) divided by h^0 we have

$$\frac{h}{h^0} = \frac{h_A{}^0}{h^0}\,[\exp(-k_A t) - \exp(-k_B t)] + \exp(-k_B t)$$

and for a given value of t·

$$h_A{}^0 = \frac{h - Dh^0}{C}$$

where:

$$C = \exp(-k_A t) - \exp(-k_B t); \qquad D = \exp(-k_B t).$$

C and D are constant for a given mixture, once temperature and time have been fixed. The choice of the most suitable time value is made on the basis of the values of k_A and k_B:

$$t_{optimum} = \frac{2{\cdot}3 \log(k_A/k_B)}{k_A - k_B}.$$

If for any reason one cannot follow the reaction to its completion—in which case the value of h^0 would not be known—then $h_A{}^0$ and $h_B{}^0$ can be computed by using two points of the experimental curve.

EXPERIMENTAL

Apparatus

The apparatus has already been described.[15] The reaction cell, which consists of a vessel with insulated walls, has on its top an insulating cover through which are inserted a stirrer, a small heating resistor (for adjusting the initial temperature), a thermistor, and a phial-breaker (or a syringe needle). The thickness and the thermal capacity of the reaction cell and the equipment contained therein are kept as low as possible in order to achieve a rapid thermal equilibration of the calorimetric system during the reaction, which is particularly necessary for the study of fast reactions. The cell is immersed in a thermostatic bath regulated to $\pm 0{\cdot}01°$. The inertia of the calorimetric system in reaching thermal equilibrium under certain conditions of mechanical agitation may be estimated by causing an instantaneous thermal event (*e.g.*, rapid injection of a few drops of a substance having a high heat of dilution) and recording the temperature change.

If a Dewar vessel with very thin walls (*e.g.*, the lightest commercial thermos has a wall thickness of about 0·5 mm) or an externally insulated metallic vessel with moderately rapid stirring (2000 rpm) is used, the response time (99% of complete change) can be less than a second. Under these conditions, kinetics for reactions with $t_{1/2}$ down to about 2 sec can be followed with an error of 1%.

For kinetics with observation times greater than several minutes, the temperature of the thermostatic bath is continuously adjusted to follow that of the reaction cell to $\pm 0{\cdot}01°$, by the use of a Wheatstone bridge with two fixed arms and two thermistors with identical characteristics, one immersed in the reaction cell and the other in the thermostatic bath. When appropriately amplified, the signal from the unbalanced bridge controls the temperature of the thermostatic bath through a proportional device.[16] With observation times of about 10 min, this device gives a reproducibility of 1%.

The thermistors (thin glass probe, fast response, 2K type) were supplied by Fenwal Electronics Inc. The voltage supply for the bridge was a 1·5-V battery. The output of the bridge (0–3 mV) was recorded on a potentiometric recorder (1-sec, 1, 2 or 5 mV f.s.d.) manufactured by Texas Instruments Inc.

Reagents

The ethyl, methyl, and isopropyl acetates were purified by standard procedures.

RESULTS AND DISCUSSION

To check the range of applicability of the equipment, measurements were made of the hydrolysis of some esters of acetic acid for which abundant rate-data exist in the literature.

Tables I–III show our data along with those of other authors, with an indication of the experimental method used in each case. It may be noted that with one exception,[6] the experimental conditions used by the other authors led to rates smaller by one or more orders of magnitude. In the same range of sodium hydroxide concentrations the best agreement was found with the data of Becker,[9] there being a rather substantial (15–20%) disagreement with those of the other authors. Such a difference might be due to an insufficiently reliable titrimetric method in the case of such fast reactions, or to insufficient accuracy of the non-adiabatic enthalpimetric method based only on the measurement of the maximum of the $\Delta T/$ *vs.* t plot. We used sodium hydroxide concentrations ranging from 0·01 to 1M and in order to get sufficiently high reaction rates, the experiments at lower concentrations were run with correspondingly higher concentrations of esters (up to 0·8M). It has been verified, however, that the second order rate constant is independent of the ester concentration.

The data show that the second-order specific rate has k_{II} increasing somewhat with increasing concentration of alkali; this increase is considerably greater than

TABLE I.—SECOND-ORDER RATE CONSTANTS FOR THE ALKALINE HYDROLYSIS OF METHYL ACETATE AT DIFFERENT CONCENTRATIONS OF NaOH, AT 25°C

Reference	Method	[Ester] *M*	[NaOH] *M*	k_{II} *mole*$^{-1}$ *l sec*$^{-1}$	$t_{1/2}$* *sec*	ΔH *kcal/mole*	E_{act} *kcal/mole*
6	thermometric non-adiabatic	0 05 — 0 4	—	0 152		−15	+10 3
22	titrimetric	0 020	0 020	0 152			+10·7
23	titrimetric	0 050	0 050	0 158			+11 95
9	conductometric	0 018	0·018	0 195		−11·92	
this paper	thermometric adiabatic	0 009 0 307	0·010 0 010	0 198 ± 1% 0·192 ± 1%			
this paper	thermometric adiabatic	0 0091	0 244	0 206 ± 1%	13 8		
this paper	thermometric adiabatic	0 0091	0 485	0 206 ± 1%	6 9	−12 0	+13 8
this paper	thermometric adiabatic	0 0091	0 971	0 206 ± 1%	3 5		

* As pseudo first-order reaction

TABLE II.—SECOND-ORDER RATE CONSTANTS FOR THE ALKALINE HYDROLYSIS OF ETHYL ACETATE AT DIFFERENT CONCENTRATIONS OF NaOH, AT 25°C

Reference	Method	[Ester] *M*	[NaOH] *M*	k_{II} *mole*$^{-1}$*.l sec*$^{-1}$	$t_{1/2}$* *sec*	ΔH *kcal/mole*	E_{act} *kcal/mole*
9	conductometric	0·018	0·018	0 116		−13 08	
23	titrimetric	0 050	0 050	0·108			+11 55
this paper	thermometric adiabatic	0 254	0·0080	0·109 ± 0 5%	26 6		
this paper	thermometric adiabatic	0 505	0 0080	0·108 ± 0 4%	12 7		
this paper	thermometric adiabatic	0 811	0 0123	0 109 ± 1%	7 9		
this paper	thermometric adiabatic	0 505	0·0145	0·112 ± 0·7%	12 5		
this paper	thermometric adiabatic	0 010	0·267	0·131 ± 0 2%	20 3		
this paper	thermometric adiabatic	0 016	0·505	0·137 ± 0 3%	10·2	−13·1	+13 1
this paper	thermometric adiabatic	0 016	1 01	0 141 ± 0·7%	4·9		

* As pseudo first-order reaction.

TABLE III.—SECOND-ORDER RATE CONSTANTS FOR THE ALKALINE HYDROLYSIS OF ISOPROPYL ACETATE AT DIFFERENT CONCENTRATIONS OF NaOH AT 25°C

Reference	Method	[Ester] *M*	[NaOH] *M*	k_{II} *mole*$^{-1}$ *l sec*$^{-1}$	$t_{1/2}$* *sec*	ΔH *kcal/mole*	E_{act} *kcal/mole*
this paper	thermometric adiabatic	0·168	0 0133	0 0276 ± 1 6%			
		$5\,98 \times 10^{-3}$	0 242	0 0363 ± 1 5%			
		$5\,98 \times 10^{-3}$	0 486	0 0390 ± 1 5%			
		$5\,98 \times 10^{-3}$	0 939	0 0403 ± 3 1%	19	−13 8	+9 1

* As pseudo first-order reaction.

TABLE IV.—SECOND-ORDER RATE CONSTANTS FOR THE ALKALINE HYDROLYSIS OF ALKYL ACETATES AT DIFFERENT TEMPERATURES

Temp °C	[Ester] M	[NaOH] M	$t_{1/2}$ sec	k_{II}* mole^{-1}.l.sec^{-1}	ΔH kcal/mole	E_{act} kcal/mole
			Methyl acetate			
19 5	0·012	0·500	9·45	0·148		
25 0	0 091	0·485	6·93	0·206	−12 0	+13·8
32·0	0·012	0·500	3·63	0·388		
			Ethyl acetate			
19·0	$1·6 . 10^{-2}$	0·505	15 9	0·088	−13 1	+13·1
25·0	$1·6 . 10^{-2}$	0·505	10·2	0·137		
32 0	$1 6 . 10^{-2}$	0·505	6·1	0·232		
			Isopropyl acetate			
25 0	$5·98 . 10^{-3}$	0 939	19 0	0·0403 ± 3·1%	−13·8	+9·1
30·0	$5·98 . 10^{-3}$	0·944	15·5	0 0492 ± 3 5%		
35·0	$5 98 . 10^{-3}$	0·942	10·7	0·0672 ± 1 0%		

* The reproducibility was ±1% or better.

might be due to experimental errors. The variation of k_{II} with concentration of alkali is not linear, however, but levels off with increasing alkali concentration.

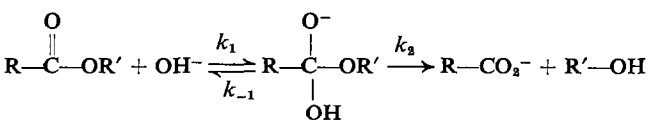
That this behaviour can hardly be a simple salt effect is shown by the data in Table V, for ester-hydrolysis reactions in solutions with varying salt concentrations. The effect is that of *decreasing* the reaction rate in an approximately logarithmic fashion as is expected for a reaction between a neutral molecule and an ion.[17] The slope in the plot of log k *vs.* [NaCl] for the hydrolysis of ethyl acetate is in agreement with the value found by Edith Schade.[18]

TABLE V.—EFFECT OF SALT CONCENTRATION ON THE ALKALINE HYDROLYSIS OF METHYL AND ETHYL ACETATE AT 25°C

Methyl acetate 0·0091*M* Sodium hydroxide 0·242*M*		Ethyl acetate 0·0121*M* Sodium hydroxide 0·502*M*		Ethyl acetate 0·505*M* Sodium hydroxide 0·0143*M*	
[NaCl] M	k_{II} mole^{-1}.l.sec^{-1}	[NaCl] M	k_{II} mole^{-1}.l.sec^{-1}	[NaCl] M	k_{II} mole^{-1}.l.sec^{-1}
0	0 206 ± 1%	0	0 137 ± 1%	0	0·112 ± 1%
0·243	0·205 ± 1%	0 493	0·128 ± 1%	0·495	0·105 ± 1%
0·487	0·202 ± 1%	0·985	0·120 ± 0 3%	0 990	0·0985 ± 1%
0·731	0·192 ± 1%	1·485	0 112 ± 0·5%		

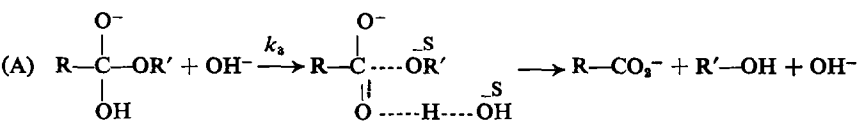
The paucity of experimental data does not permit us to put forward a proven mechanistic interpretation of the effect of high concentrations of alkali, but a mechanism can be suggested.

It is well known that the saponification of esters proceeds through addition of OH^- to the carbonyl group leading to a tetrahedral intermediate which can either decompose to alcohol and carboxylic acid or revert to starting material.[19]

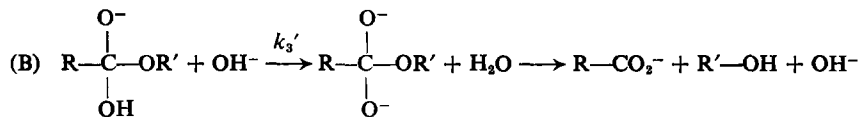


I

The fact that ^{18}O-exchange between the aqueous solvent and the carbonyl group of the unreacted ester takes place at a rate comparable to the saponification rate, clearly indicated that the decomposition steps of intermediate **I** effectively compete with each other (*i.e.*, k_{-1} and k_2 are of the same order of magnitude). Under such circumstances, an additional contribution to the rate may be expected in more concentrated alkali. This would be a base-promoted proton abstraction from **I** leading to products in a single concerted step (A), or by way of a second intermediate, **II**, which in turn may either yield the products or revert to **I**.



I



II

This hypothesis is not unreasonable in view of the following.

(*a*) Ester hydrolysis is known to undergo general base catalysis,[20] an observation requiring an explanation similar to that offered here.

(*b*) A third-order contribution, second-order in $[OH^-]$, has been found by Taft[21] in the alkaline hydrolysis of trifluoroacetanilide and has been explained on the same basis. Actually, Taft proposed the formation of a doubly-charged anion as a second intermediate (mechanism B). It is clear, however, that the concerted process A alternatively proposed here would be indistinguishable from B on the basis of the facts now available.

(*c*) Finally, as the data of Tables I–III show, the increase of k_{II} with increasing hydroxyl ion concentration becomes greater in the order: methoxide < ethoxide < isopropoxide, *i.e.*, in the inverse order of mobility of the leaving group*; the contribution that this additional path makes to the total rate is expected to become relatively more important the "harder" the leaving group since the "spontaneous" decomposition path of intermediate **I** (k_2) becomes relatively less important.

We feel that the rationalization offered here is a working hypothesis more than an explanation, and much more experimentation is needed in order to provide it with a sound factual basis.

To examine the possibility of using the apparatus for kinetic chemical analysis, we studied the model system of methyl acetate and isopropyl acetate at different ratios of ester concentration. The results, calculated in accordance with the preceding paragraph, are reported in Table VI; they show the applicability of the method for the rapid analysis of mixtures or, similarly, for the study of consecutive reactions.

In this case, too, the contribution due to the heat of dilution (and thus to the stirring speed) does not have a critical influence on the accuracy. For the experiment reported in Fig. 2, for example, the mixture of esters was purposely introduced at a temperature lower than that of the solution. In addition, the stirring speed used was only 1500 rpm. Examination of curve *d* in Fig. 2 shows that there was an initial drop in temperature quickly compensated for by the development of the heat of reaction. This low stirring speed allows a reading of the first useful point only after 3 sec, when about 40% of the more reactive compound has already reacted; in addition, the negative thermal contribution during the mixing makes the height h^0 indeterminate. In each

* That the order of leaving group mobility is $MeO^- > EtO^- >$ iso-PrO^- seems reasonable on the basis of the inductive effect of alkyl groups. It is also experimentally supported by the fact that in the ^{18}O experiments the ratio k_{ex}/k_{hydr} increases when going from ethyl to isopropyl esters.

TABLE VI.—KINETIC DIFFERENTIAL ANALYSIS FOR THE MODEL SYSTEM ISOPROPYL ACETATE/METHYL ACETATE

Methyl acetate			Isopropyl acetate		
Theory	Found	Difference	Theory	Found	Difference
mmole		%	*mmole*		%
	0·659			0·667	
	0 648			0·675	
0·666	0·649	2·2	0 666	0·650	0·9
	0·650			0·650	
	av. 0·651 ± 0·6%			av. 0·660 ± 1·6%	
	0·417			0·855	
	0·408			0·857	
0·424	0·421	1·9	0·848	0·834	0·3
	0·417			0 833	
	av. 0·416 ± 0 9%			av. 0.845 ± 1·3%	
	0·584			0·841	
0·561	0·526	0·3	0·850	0·871	0·5
	0·580			0·850	
	av. 0·563 ± 4%			av. 0·854 ± 2%	

case, the value of the heights h relative to each of the components—obtained through extrapolation of the curves a and b—was in excellent agreement with the theoretical data.

CONCLUSION

The quasi-adiabatic thermal method represents a powerful tool for the study of moderately fast reactions ($t_{1/2}$ down to 2 sec). Consecutive reactions or differential kinetic analysis can be followed with good accuracy and reproducibility, and the results are not critically affected by changes in the experimental conditions.

Zusammenfassung—Die quasiadiabatische und die nichtadiabatische thermometrische Methode werden hinsichtlich ihrer Anwendung auf die chemische Kinetik verglichen. Mit Thermistoren als Temperaturfühlern und einer sehr einfachen Apparatur konnen ziemlich schnelle Reaktionen (mit Halbwertszeiten bis herunter zu 2 sec) und Folgereaktionen verfolgt sowie Mischungen mit guter Genauigkeit analysiert werden. Die Reproduzierbarkeit ist in einem weiten Bereich experimenteller Bedingungen zufriedenstellend. Die Berechnung der kinetischen Parameter ist für erste und zweite Ordnung sehr einfach und erfordert keine Eichung des Systems. Die Anwendung des Verfahrens auf die alkalische Hydrolyse einiger Alkylacetate wird beschrieben.

Résumé—On compare les méthodes thermiques quasi-adiabatique et non-adiabatique pour l'étude des cinétiques chimiques. Avec des thermistors pour éléments sensibles à la température et un appareil très simple, on peut suivre des réactions modérément rapides (avec $t_{1/2}$ descendant jusqu'à 2 sec) et des réactions consécutives et analyser des mélanges avec une bonne précision. La reproductibilité est satisfaisante dans un large domaine de conditions expérimentales. Le calcul des paramètres cinétiques, pour les cinétiques d'ordre un et deux, est très simple et ne nécessite pas d'étalonnage du système. On décrit l'application de la technique à l'étude de l'hydrolyse alcaline de quelques acétates d'alkyle.

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1-HYDROXY-ETHYLIDENE-1,1-DIPHOSPHONIC ACID AS A TITRIMETRIC AGENT

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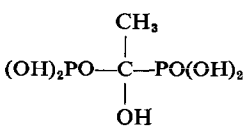
Summary—1-Hydroxy-ethylidene-1,1-diphosphonic acid (HEDPHA) has been proposed as a highly selective titrimetric reagent for thorium. In the presence of 1,2-diaminocyclohexanetetra-acetic acid (DCTA) a soluble binuclear ternary complex, $Th_2(DCTA)_2(HEDPHA)$, is formed. The determination of thorium is carried out in a slightly acidic medium, buffered with urotropine, with 0·025*M* HEDPHA, and Xylenol Orange as indicator. DCTA masks all bivalent metals, rare earths, scandium, yttrium, bismuth, iron, gallium and indium. Only zirconium, titanium, aluminium and large amounts of thallium(III) interfere.

IN ONE of our previous papers[1] we paid attention to the determination of light lanthanides in the presence of erbium, thulium and ytterbium. The method is based on the displacement reaction:

$$LnY^- + Zn^{2+} + PO_4^{3-} = ZnY^{2-} + LaPO_4 \qquad (1)$$

where Ln = La, Ce, Pr, Nd; Y = anion of EDTA. These titrations are performed in urotropine-buffered medium at pH 5–5·5 with Xylenol Orange as indicator. Reaction (1) is quantitative and fast enough for analytical purposes only for light lanthanides. Some other rare earths react slowly with phosphate but erbium, thulium and ytterbium do not react at all. Recently our study has been extended to other titrants (DCTA, DTPA, TTHA, *etc.**) and other complex-forming agents such as pyrophosphate and fluoride. From our experiments we obtained a very different picture about the reaction (1). For example the thorium complex of TTHA does not react with phosphate during the zinc titration, whereas the scandium complex does.[2] DTPA complexes of rare earths are not displaced during the zinc titration in the presence of phosphates. On the contrary, all rare earths can be determined by back-titration of DTPA with zinc even in the presence of phosphates.[3] TTHA complexes of lanthanum, cerium and praseodymium are displaced very slowly or not at all by zinc according to reaction (1), whereas the heavier lanthanides are displaced quantitatively. Details will be published soon.

The complex-forming properties of 1-hydroxy-ethylidene-1,1-diphosphonic acid (HEDPHA), which might have been expected to act in a way similar to orthophosphate, are described below.



HEDPHA

The free acid behaves as a dibasic acid when titrated to the Methyl Red end-point and as a tribasic acid when titrated to the phenolphthalein end-point. Its efficiency

* DCTA = 1,2-diaminocyclohexane-*N,N,N′,N′*-tetra-acetic acid
DTPA = diethylenetriamine-*N,N,N′,N′,N″*-penta-acetic acid
TTHA = triethylenetetramine-*N,N,N′,N″,N‴,N‴*-hexa-acetic acid.

in masking bivalent cations from Xylenol Orange is very low, but aluminium, iron(III) and titanium are masked completely, though in their presence poor end-points are obtained in the titration of bivalent metals such as zinc and lead. The complexes of iron(III) with EDTA and DCTA do not react with HEDPHA, but the corresponding aluminium and titanium complexes do to some extent. In acidic medium it precipitates thorium, scandium and rare earths. The precipitation of thorium and scandium can be followed with Xylenol Orange as indicator; the precipitation of scandium gives a very sharp end-point.

It is well-known that thorium EDTA or DCTA complexes, even in the presence of excess of complexing agents react at above pH 4 with various metallochromic indicators such as Xylenol Orange or Methylthymol Blue, to give a ternary complex ThY-X which is red in colour, displacing hydroxide ion from the complex ThOHY, which is formed at this pH in the absence of suitable ligands ($\log K^{OH}_{ThOHY} = 7$).

In preliminary experiments we have titrated solutions of Th-EDTA or Th-DCTA (prepared by titration of thorium with EDTA or DCTA at pH 2·5–3·5) with HEDPHA solution, Xylenol Orange being used as indicator. The solutions were well buffered with urotropine before the start of the titration. All the solutions remained clear without any traces of cloudiness and the end-point with Xylenol Orange was sufficiently sharp provided that the titration was performed slowly and with intense stirring. The consumption of HEDPHA was exactly half a mole for one mole of thorium. This is not in agreement with the direct titration of thorium in acidic medium (without EDTA or DCTA) in which a precipitate of 1:1 composition is formed. We have also found that the complexing agent is not liberated at all from the Th-EDTA or Th-DCTA complex during the titration with HEDPHA. This difference in behaviour indicates that the complexing agent takes part in this titration. We assume that a binuclear ternary complex of the structure (I) is formed according to the reaction:

$$2ThY + H_4CP_2O_5 = Th_2Y_2(CP_2O_5)^{4-} + 4H^+ \qquad (2)$$

or

$$2ThY + CP_2O_5^{4-} = Th_2Y_2(CP_2O_5)^{4-} \qquad (3)$$

where CP_2O_5 is an anion of HEDPHA

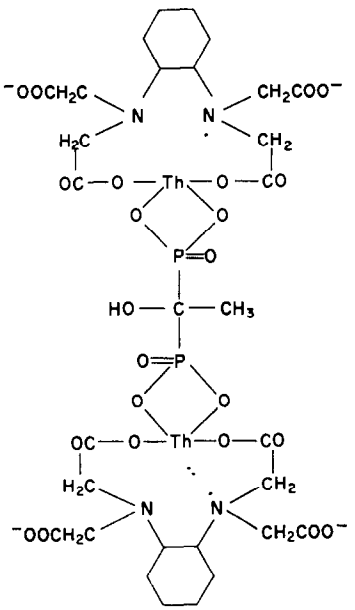
The existence of such a complex has been confirmed by acid-base titrations of mixtures of thorium–EDTA (or –DCTA) complex and HEDPHA in the ratio 2 ThY : 1 HEDPHA. It is analogous to the binuclear Xylenol Orange complex,[6] $Th_2Y_2(XO)_2$, whose existence is indicated by spectrophotometric and biamperometric titrations.

Our findings prove also the existence of a ternary complex of thorium with Xylenol Orange at above pH 4. At the end-point (colour change from red-violet to yellow or orange-yellow) such a reaction might exist:

$$2ThY\text{–}XO + CP_2O_5 = Th_2Y_2(CP_2O_5) + 2XO \qquad (4)$$

red violet yellow

(charges are omitted).



(I)

These findings led to a study of the experimental conditions which would enable thorium to be determined titrimetrically with HEDPHA in the presence of DCTA or EDTA which would serve as a masking agent for other elements.

EXPERIMENTAL

Reagents

Thorium nitrate solution, 0·05*M*. Dissolve 27·66 g of $Th(NO_3)_4.4H_2O$ in 100 ml of 1*M* nitric acid and dilute to 1 l.

DCTA, 0·05*M*. Dissolve 17·8 g of 1,2-diaminocyclohexanetetra-acetic acid in 100–120 ml of 1*M* sodium hydroxide with slight warming. Allow to cool and dilute to 1 l.

DTPA, 0·05*M*. Dissolve 19·65 g of diethylenetriaminepenta-acetic acid in 100–120 ml of 1*M* sodium hydroxide with slight warming. Allow to cool and dilute to 1 l.

Zinc nitrate solution, 0·05*M*. Dissolve 2·2685 g of metallic zinc in 40 ml of nitric acid (1 + 1) and dilute to 1 l.

HEDPHA, 0·025*M*. Dissolve 5·5–5·8 g of 1-hydroxyethylidene-1,1-diphosphonic acid in 100 ml of water. Adjust the pH of the solution with 1*M* sodium hydroxide to 4·5–5 (indicator paper) and dilute to 1 l. The sample used (Albright and Wilson) contained 7·74% of water (determined by drying to constant weight at 110°).

Urotropine solution, 20%.

Nitric acid, approx 1*M*.

Sodium hydroxide, approx 1*M*.

Xylenol Orange solution, 0·5% *aqueous*.

Standardization of the solutions

Zinc nitrate solution (0·05*M*) serves as a standard. Solutions of DCTA and DTPA are standardized complexometrically with zinc, at pH 5–5·5, (urotropine buffer), Xylenol Orange being used as indicator. The thorium nitrate is standardized by DCTA titration at pH 3, with Xylenol Orange as indicator. HEDPHA is standardized as follows. Place 5 ml of 0·05*M* thorium nitrate in a 250-ml beaker, add 6–7 ml of 0·05*M* DCTA and dilute to 100–120 ml. Add a few drops of Xylenol Orange, buffer the solution with urotropine solution to give a red-violet colour and add a further 10 ml. Titrate this solution with 0·025*M* HEDPHA from red-violet to orange-yellow. Calculate the titre according to the relationship 1 ml 0·05*M* $Th(NO_3)_4 \equiv$ 1 ml 0·025*M* HEDPHA.

Solutions (0·05*M*) of various metals, *viz.*, various rare earths, Fe, Bi, Zr, Al, Ga, In, Tl(III), Ti, Sc, Y, Ni, Cu, Cd, Zn), were prepared from reagent grade chemicals and standardized complexometrically.

Procedures

Determination of thorium, preliminary experiments. From 5 to 10 ml of 0·05*M* solution of thorium nitrate were diluted to 100–120 ml and the pH adjusted to 2·5–3 5 with 1*M* nitric acid or 1*M* ammonia solution or urotropine solution. A few drops of Xylenol Orange were added and the solution titrated with 0·05*M* EDTA or DCTA from red-violet to lemon-yellow and a small excess of the titrant was added. Then urotropine was added to give a red-violet colour, and then 10 ml extra were added The resulting pH of the solution was 5–6. This solution was slowly titrated with 0·025*M* HEDPHA from red to orange-yellow. The end-points were sufficiently sharp and corresponded to accurate consumption, *i.e.*, 1 ml 0·025*M* HEDPHA ≡ 1 ml 0·05*M* $Th(NO_3)_4$ (from the first titration).

Similar titrations have been carried out with varying amounts of excess of DCTA. It is found that up to a 9-fold excess of DCTA does not influence the end-point and accuracy provided that not more than 120 mg of it is present. The results are summarized in Table I.

Xylenol Orange is suitable for this titration, but with Methylthymol Blue the colour change comes before the end point.

Determination of thorium in the presence of other metals. Preliminary experiments showed that EDTA is not suitable for masking. Some EDTA-complexes reacted slightly with HEDPHA and the results were higher for thorium than expected. For this reason DCTA, which forms more stable complexes than EDTA, has been used for all experiments. Because the end-point of HEDPHA

TABLE I.—DETERMINATION OF THORIUM WITH HEDPHA IN THE PRESENCE OF DCTA

Thorium taken, *mg*	DCTA, 0 05*M*, *ml*	Mole ratio DCTA Th	HEDPHA, 0 025*M*, *ml*	Thorium found, *mg*	Difference, *mg*
12 12	2·00	2:1	1·07	12 41	+0 29
12·12	10 00	10.1	1·05	12 18	+0·06
12·12	50 00	50:1	0·90–1·10*	—	—
24·24	5·00	5 2	2 10	24·36	+0·12
24 24	10·00	5·1	2 10	24 36	+0.12
24 24	50·00	25·1	2 00–2 10*	—	—
84·83	10·00	10:7	7 27	84 35	−0 48
84 83	50·00	50 7	7·20–7 40*	—	—
121·18	12·00	6.5	10·42	120·90	−0 28
121·18	50·00	5·1	10·50–10·80*	—	—

* End-point vague, too much DCTA used.

TABLE II.—DETERMINATION OF THORIUM IN THE PRESENCE OF OTHER METALS

Taken		DCTA,	HEDPHA,	Thorium	
Th, *mg*	Me, *mg*	0 05*M*, *ml*	0·025*M*, *ml*	found, *mg*	Difference, *mg*
12·12	35 La	10 00	1·07	12 41	+0·29
6·06	70 La	15·00	0 55	6 38	+0 32
36·36	70 La	15·00	3 07	35·62	−0 74
24 24	80 Tb	15 00	2 07	24 02	−0·22
121·18	7 La	12 00	10 45	121 25	+0 07
12·12	40 Gd	7·00	1·05	12·18	+0·06
84·84	58 Ho	16 00	7·25	84 12	−0·72
2·42	42 Er	6·00	0·24	2·78	+0 36
6 06	348 La	56 00	0·51–0 54*	—	—
12 12	22 Sc	13 00	1 05	12·18	+0 06
36 36	7 Sc	8 00	3 12	36·20	−0 16
60·60	3 Sc	8·00	5·22	60·57	−0 03
24·24	28 Fe	14·00	2·06	23·91	−0 32
36·36	136 Bi	18·00	3 12	36·20	−0 16
24·24	18 Ga	9·00	2·10	24·36	+0 12
36·36	58 In	15 00	3·12	36 20	−0·16
121 18	32 Cu	25 00	10·44	121 15	−0 03
24·24	33 Ni	15 00	2 10	24 36	+0 12

* Vague end-point, too much La present

titrations is sharpest if not too great an excess of free DCTA is present, the amount of other elements present has to be known. Their complexometric determination with EDTA or DCTA is impossible, because thorium interferes forming a coloured complex with Xylenol Orange (see above), but DTPA can be used.[4] Therefore for the determination of thorium two aliquots of the sample solution are necessary.

(*a*) *Determination of the sum of metals.* Add to a suitable aliquot an excess of 0·05*M* DTPA, dilute to 100–120 ml, add a few drops of Xylenol Orange, adjust the pH to 5–5 5 with urotropine and titrate with 0 05*M* zinc nitrate from lemon-yellow to red-violet.

(*b*) *Determination of thorium.* To the second aliquot in a beaker add the same volume of 0·05*M* DCTA as the DTPA consumed in titration *a* and then 1–3 ml in excess. Dilute to 100–120 ml, add Xylenol Orange and then urotropine till a red colour appears. To ensure good buffer capacity add 10 ml of urotropine in excess. Stir magnetically and titrate slowly with 0 025*M* HEDPHA from red to orange-yellow.

RESULTS

As can be seen from Table II a number of metals do not interfere, because they are firmly bound with DCTA. Only zirconium, titanium, aluminium and large amounts of thallium (III) interfere. Because of the partial reaction with HEDPHA the EDTA and DCTA complexes of these metals, the end-points are very indistinct and the titrations fail completely.

Acknowledgement—One of us (R. P.) expresses his heartiest thanks to Dr. A. F. Childs, Head of Research Department, Albright and Wilson (Mfg) Ltd., Oldbury, Birmingham, for the warm reception during his stay in Birmingham and for the gift of HEDPHA and other chemicals.

Zusammenfassung—1-Hydroxyathyliden-1, 1-diphosphonsäure (HEDPHA) wurde als hochselektives titrimetrisches Reagens für Thorium vorgeschlagen. In Gegenwart von 1,2-Diaminocyclohexantetraessigsäure (DCTA) wird ein löslicher zweikerniger ternarer Komplex $Th_2(DCTA)_2(HEDPHA)$ gebildet. Die Thoriumbestimmung wird in schwach saurem, mit Urotropin gepuffertem Medium mit 0,025*M* HEDPHA und Xylenolorange als Indikator ausgeführt. DCTA maskiert alle zweiwertigen Metalle, seltene Erden, Scandium, Yttrium, Wismut, Eisen, Gallium und Indium. Nur Zirkonium, Titan, Aluminium und große Mengen Thallium(III) stören.

Résumé—On a proposé l'acide 1-hydroxy éthylidène 1,1-diphosphonique (HEDPHA) comme réactif titrimétrique hautement sélectif du thorium. En presence d'acide 1,2-diaminocyclohexane tétracétique (DCTA), il se forme un complexe binucléaire ternaire soluble, $Th_2(DCTA)_2$-(HEDPHA). Le dosage du thorium est mené en milieu légèrement acide, tamponné à l'urotropine, avec HEDPHA 0,025*M* en présence de Xylénol Orangé comme indicateur. Le DCTA dissimule tous les métaux bivalents, les terres rares, le scandium, l'yttrium, le bismuth, le fer, le gallium et l'indium. Seuls le zirconium, le titane, l'aluminium et de fortes quantités de thallium(III) gênent.

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DETERMINATION OF MICROGRAM QUANTITIES OF TIN(IV) BY A COMBINED ION-EXCHANGE/X-RAY FLUORESCENCE TECHNIQUE

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Summary—A method is described for the analysis of microgram quantities of tin in dilute hydrofluoric acid. The tin is extracted onto anion-exchange resin loaded paper discs by a very simple technique and the papers are examined by X-ray fluorescence spectrography. The solutions are obtained by the dissolution of tin-containing glasses, and the normal glass-forming elements do not interfere. The method is intended for the determination of 1–20 μg of tin but may be used for up to at least 250 μg; 5 μg can be determined with a precision of $\pm 10\%$

A METHOD was required for the determination of microgram amounts of tin in small quantities of 1% hydrofluoric acid. These solutions were obtained by etching tin-containing glasses. Attempts at the direct analysis of these solutions by X-ray fluorescence spectrography failed because of inadequate sensitivity. It was thought that a concentration or separation technique could be applied to increase the sensitivity to a satisfactory level. Among the methods considered were: the ring oven technique; extraction of tin into an organic solvent followed by evaporation; extraction onto an ion-exchange membrane or paper.

The third method was thought to be the simplest and cleanest. This technique has been used by other workers for the determination of trace quantities of many metals. Cation-exchange membranes and papers have been used with success for concentrating impurities in tungsten and molybdenum after separation from the major constituents.[1–5] The impurities (aluminium, calcium, chromium, cobalt, copper, iron, lead, manganese, nickel and zinc) dissolved in hydrochloric acid at pH 2, were collected by passing the solution through the ion-exchange paper a number of times in order to achieve equilibrium. The overall precision of the method was $\pm 10\%$.

Information on the use of anion-exchange membranes and papers is less comprehensive and to some extent conflicting. Lytle, Dye and Seim,[6] when investigating the uptake of molybdenum, zinc, gallium, copper, cobalt, iron, tin and bismuth, found that in no case was the transfer quantitative and that they were unable to obtain reproducible results. The membranes had been immersed in the solutions and agitated for some hours. Minns,[7] however, describes the successful extractions of chromium as chromate, and mercury and platinum as chloride complexes, by a filtration technique. Link and co-workers[8] were also able to separate mercury by a similar procedure and attained a precision of $\pm 25\%$ at the 1-μg level. A liquid anion-exchanger[9] has been used for the estimation of trace quantities of uranium.

EXPERIMENTAL

Apparatus

Beakers. Squat 100-ml polypropylene beakers (5 cm diameter, 6 cm high).

X-ray fluorescence. Philips PW1540 Universal all-vacuum spectrograph Tube: chromium target operated at 48 kV, 18 mA. Analysing line: SnLα (3 60 Å). Analysing crystal: LiF ($2d = 4{\cdot}028$ Å). Detector: flow proportional counter using argon–methane P10 mixture and pulse-height analyser. Collimator: coarse (480 μ). Exposure time· 50 sec.

Reagents

Hydrochloric acid (analytical reagent grade).

Ion-exchange paper. Rohm and Haas SB-2 anion-exchange paper. Cut circles of this paper with a circular punch of the correct diameter ($1\frac{5}{16}$ in.) to fit the standard sample holder of the spectrograph.

Tin solution. Dissolve 1·000 g of analytical reagent grade tin in 100 ml of hydrochloric acid (1 + 1) and fully oxidize it by passing chlorine or oxygen through the solution. Boil to expel excess of gas, cool, add 300 ml of concentrated hydrochloric acid and make to 1 l. with deionized water. Dilute this solution as required, always maintaining the acid concentration at 4*M* to prevent hydrolysis.

Procedure

Place in the beaker 10 ml of the 1% hydrofluoric acid containing the tin. Add 11 ml of concentrated hydrochloric acid and 4 ml of deionized water, making the solution 6*M* with respect to hydrochloric acid, then immerse a circle of anion-exchange paper in it for 18 hr Carefully remove the paper with acid-resistant tweezers and dry it for 2 hr in a fan oven at 45–50°. Mount the paper in the sample holder of the spectrograph by means of a rubber O-ring Fully evacuate the spectrograph and compare all samples with a single reference in order to obtain the ratio $I_{sample}/I_{reference}$ for each sample. Compare these ratios with the calibration graph obtained from standard tin solutions processed in a like manner

DISCUSSION

SB-2 ion-exchange paper, manufactured by Rohm and Haas, contains Amberlite IRA-400 anion-exchange resin which owes its activity to strongly basic quaternary ammonium groups. Dowex-1 is an equivalent resin and has been used by Nelson, Rush and Krauss[10] in their extensive investigations into the effect of hydrochloric and hydrofluoric acids on the distribution coefficients of many elements. The results quoted by Nelson *et al.* indicate that the optimum hydrochloric acid concentration for the extraction of tin(IV), in which form the tin is present, is 4*M*. Hydrochloric acid was chosen for the present work in preference to hydrofluoric acid because it is less obnoxious.

Filtration of the solutions through the papers and suspension of the papers in the agitated solutions were considered but were never put into operation because the procedure above was found to be so successful. A few preliminary experiments showed that a suitable quantity of solution in which to immerse the paper was 25 ml in a standard 100-ml squat beaker. It was also found that 25 ml could be employed in a 250-ml squat beaker but not in a 100-ml tall beaker. It seemed that the uptake of tin was some function of the depth of solution above the paper, and that if the depth were too great the uptake was low. The nature of this function was not investigated since it was such an easy matter to standardize the procedure. It was also found that the tin counts on the two sides of the paper were different; the mean value was taken.

It must be emphasized that although the papers are cut to fit snugly in the sample holder, the whole paper is not scanned by the X-ray beam. Clearly the conditions of uptake must be such that the tin is reproducibly distributed over each of the two surfaces of the paper. In order to establish this, papers were immersed in 50-μg standards in 4*M* hydrochloric acid, as recommended by Nelson *et al.* and removed at different times From Fig. 1 it can be seen that the averaged count from the papers

alters by a relatively small amount during an extended immersion. On the other hand the distribution of the tin alters markedly. Initially the top surfaces bear much more tin. This difference decreases until, after about 60 hr, the two surfaces are equivalent. After this the top surface still appears to lose tin and the lower to gain it. It would appear that the optimum immersion time is probably about 60 hr but this is not exactly an ideal time for a rapid analytical method. Eighteen hours may be regarded as a convenient overnight period and tests of reproducibility showed that satisfactory results could be obtained in this time. The standard deviation for ten 50-μg samples was found to be 1·7 μg and it is inferred that a reproducible

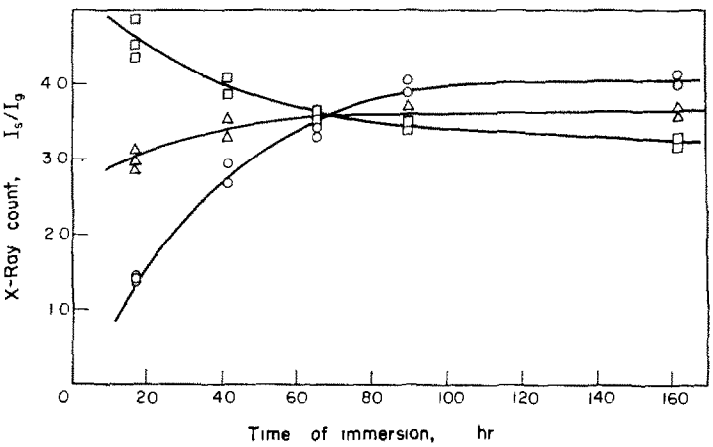

FIG. 1.—Distribution of the tin on the paper.
□—Top surface; ○—bottom surface; △—mean.

distribution over the surfaces is achieved. Measurement of one of these samples ten times indicated the standard deviation of the spectrographic measurements to be 0·7 μg.

The optimum concentration of hydrochloric acid was determined for three ranges of solutions: hydrochloric acid alone, hydrochloric acid/0·4% hydrofluoric acid (*i.e.*, 10 ml of 1% hydrofluoric acid diluted to 25 ml as in procedure), and hydrochloric acid/1% hydrofluoric acid. It can be seen from Fig. 2 that if the concentration is taken to be 6*M* then relatively wide limits may be tolerated for the concentration of hydrofluoric acid. It was found that the concentration of hydrochloric acid could not be raised above 8*M* without seriously affecting the mechanical strength of the paper.

One further point was investigated, namely the efficiency of extraction. Circles of paper were immersed in 50-μg standards for 18 hr. These papers were removed and replaced by fresh ones, which were also left for 18 hr. The process was repeated twice more. A simple extrapolation of the results shows that about 70–75% of the tin is extracted. That about 30% of the tin remains in solution is probably a major contributing factor favouring reproducibility. There is no reason to suppose that a dynamic equilibrium does not exist between solution and paper and, if the reaction is allowed full rein for sufficiently long, a uniform distribution should result. The satisfactory standard deviations indicate that 18 hr are sufficiently long to establish this over each surface

Some solutions may contain as much as 2 mg of dissolved glass; it was shown that up to 10 mg produced no noticeable interference.

Tin may also be extracted from 1–10*M* hydrofluoric acid, but silicon is also extracted and causes some interference in the measurement. Thus, besides being a particularly unpleasant reagent, hydrofluoric acid is in fact detrimental to the analysis.

Elements of medium atomic number have two spectra, K and L, which are suitable for analytical purposes. Unfortunately the K spectrum of tin, although the more intense, is masked by the very high background radiation due to the scattered continuum from the tube. On the other hand, the SnLα wavelength (3·6 Å)

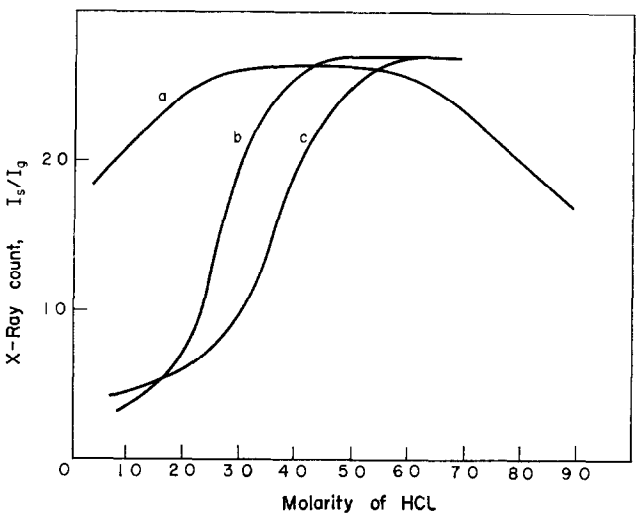

FIG. 2.—Effect of HCl concentration on tin uptake.
(*a*) No HF; (*b*) 0·4% HF; (*c*) 1 0% HF.

is appreciably absorbed by air so that either a hydrogen, helium or vacuum path is essential for maximum intensity.

Ion-exchange papers are more suitable than membranes for use in a totally evacuated system because of their greater mechanical strength and their ability to withstand drying without ill-effect. They also exhibit, in common with membranes[11,12] and filter papers,[13] the property of producing low background counts.

As temperature changes cause expansion of the analysing crystal, this and other less obvious factors can be responsible for a drift in intensity measurements during a series of analyses at this level. All samples were therefore compared to a reference (one side of a 50-μg standard) and the ratio $I_{\text{sample}}/I_{\text{reference}}$ was used throughout.

The calibration graph exhibits a slight upward curve from 0–25 μg but is then linear to at least 250 μg. The standard deviations computed at three levels, 3 μg, 7·5 μg and 15 μg, were 0·21, 0·29 and 0·42 μg respectively. The determination limit for simulated solutions is 0·2 μg but for practical solutions it is probably about 0·5–1 μg.

Résumé—On décrit une méthode pour l'analyse de quantités d'étain de l'ordre du microgramme dans l'acide fluorhydrique dilué. On extrait l'étain sur des disques de papier chargés de résine échangeuse d'anions par une technique très simple et examine les papiers par spectrographie de fluoresence aux rayons X. On obtient les solutions

par dissolution de verres contenant de l'étain, et les éléments normaux constitutifs du verre n'interfèrent pas. La méthode a pour but la détermination de 1–20 μg d'étain mais peut être utilisée jusqu'à 250 μg au moins; on peut doser 5 μg avec une précision de $\pm 10\%$.

Zusammenfassung—Ein Verfahren zur Bestimmung von Mikrogrammengen Zinn in verdunnter Flußsaure wird beschrieben. Zinn wird sehr einfach in mit Anionenaustauscherhatz beladene Papierscheiben extrahiert und die Papiere rontgenfluoreszenzspektrographisch untersucht. Die Lösungen entstehen beim Auflosen zinnhaltiger Glaser; die üblichen glasbildenden Elemente sören nicht. Das Verfahren ist entworfen zur Bestimmung von 1–20 μg Zinn, kann aber bis wenigstens 250 μg gebraucht werden; 5 μg konnen mit einer Genauigkeit von $\pm 10\%$ bestimmt werden.

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SHORT COMMUNICATIONS

Spectrophotometric determination of Channel Black in small arms propellants

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CHANNEL BLACK is frequently added to small arms propellants to act as an opacifying agent. It is preferred to other carbon blacks for this purpose because it has a very small particle size (about 9–17 mμ).

Channel black in small arms propellants is usually determined by dissolving the sample in nitric acid or a mixture of potassium hydroxide and hydrogen peroxide, followed by filtration through a Gooch crucible, drying at 120–130°, weighing, igniting at 600–650°, and calculating the loss in weight to be Channel Black.[1,2,3] This method is inaccurate because Channel Black may be attacked by the dissolution agent, lost as a colloid, or contaminated with other insoluble materials, and because the asbestos may change in weight between weighings. A spectrophotometric method has been proposed that depends on the black colour obtained when the propellant is dissolved in a mixture of acetone and acetic acid.[1] This method is subject to many errors, since the colour is due to a suspension. Also, the brand of Channel Black used in the preparation of the calibration curve must be the same as in the sample.

This laboratory has developed a spectrophotometric method that makes use of the yellow colour obtained when Channel Black is dissolved by boiling with nitric acid for 3 hr.

EXPERIMENTAL

Apparatus and reagents

Treated asbestos. Asbestos fibre, washed twice with hydrochloric acid, was filtered off and stored under water.[4]

Spectrophotometer. A Beckman Model B was used, with 1 00-cm cells.

Filter crucibles. No 4A sintered crucibles by Coors.

Method

Prepare a filter crucible by pouring into it a fairly thick suspension of treated asbestos in water, applying suction until the water has drained, and then repeating the treatment with another portion of asbestos, so as to form a pad ¼-in. thick. Wash it with water and ignite it in a muffle at 800° for 40 min.

Transfer 5 g of the propellant to a 250-ml beaker and add 60 ml of morpholine. If the propellant is finely divided, cool the morpholine in an ice-bath before adding it, in order to prevent a possibly vigorous reaction Cover with a watch-glass, insert a stirring rod, and warm on an electric hot-plate under a hood with occasional stirring until the sample is in solution (15–30 min). Heat to incipient boiling (white fumes will appear) and filter *while hot* through the filtering crucible. Wash the beaker and crucible with hot morpholine, then wash well with acetone and hot water. Empty the suction flask and add about 200 ml of tap water (to act as a trap for the hydrogen chloride evolved in the next step). Wash with hot hydrochloric acid (about 80°) and then with hot water.

Detach the pad from the crucible, and transfer the pad and crucible to a 500-ml tall-form beaker (with a lip). Add 145 ml of nitric acid, cover with a tightly fitting watch-glass, heat to boiling, and boil gently for 3 hr, swirling the solution occasionally. The volume at the end of the boiling period should be 50–70 ml. If the volume after 2 hr is greater then 80 ml, remove the watch-glass (there is no danger of loss from the tall-form beaker).

Dilute to about 175 ml with water, filter through a Whatman No 42 filter paper into a 250-ml standard flask, washing with nitric acid (1 + 9), cool the filtrate to room temperature and dilute to the mark with water and mix. Measure the absorbance at 400 mμ against water

A calibration curve may be prepared by treating approximately 10, 15, 20 and 25-mg portions (weighed to 0 1 mg) of Channel Black with morpholine and proceeding as in the method.

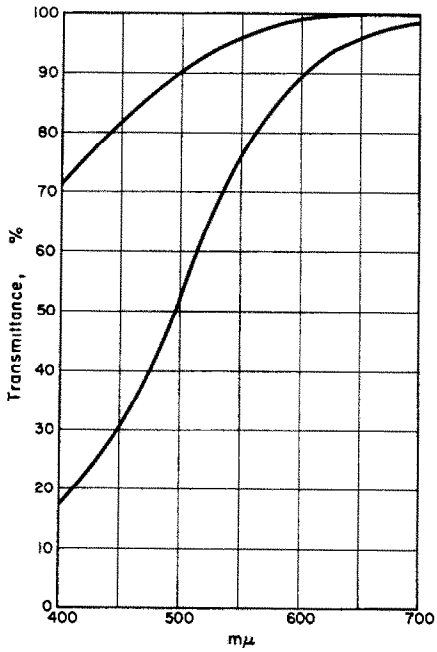

FIG. 1.—Transmission spectrum of coloured oxidation product.

RESULTS AND DISCUSSION

During the initial boiling of the nitric acid with the Channel Black, the colour may seem more intense because of the nitrogen dioxide produced. Once developed the colour is very stable and does not change on standing overnight. The transmission spectrum over the range 400–700 mμ is shown in Fig. 1. Measurement of the absorbance at 400 mμ would seem satisfactory. Beer's law is obeyed. The sensitivity is not very high, so a 5-g sample is used, giving a lower sampling error. Any sample of Channel Black can be used in preparing the calibration curve. The curves obtained with 5 different samples (Carbolac 1, Carbolac 2, Royal Spectra, Spheron 6, and Monarch 74) did not differ significantly.

The colour is due to polycarboxylic acids with cyclic nuclei. Ruof, Entel, and Howard[5] studied the colour but not from an analytical point of view. They refluxed 200 g of Channel Black with nitric acid for 11 days and found that the molecular weight of the resultant yellow carboxylic acid, determined ebullioscopically in acetone, was about 484 and that there were 6 2 carboxyl groups per molecule of carboxylic acid. The mechanism of formation of polycarboxylic acids from Channel Black involves the oxidation by the nitric acid of the peripheral rings of the polyaromatic structure of the Channel Black.

Morpholine was used by us because it was the only solvent that would dissolve 5 g of a nitrocellulose-base propellant and permit a fairly rapid filtration. The maximum sample size that could be used with 60 ml of acetone without clogging the filter was 1 g. It was found necessary to wash the carbon black, after the morpholine filtration, with acetone to remove residual nitrocellulose and other organic contaminants, then with hot water to remove soluble salts (nitrates, perchlorates, sulphates, *etc.*), and finally with hot hydrochloric acid to remove organic lead salts, barium chromate, nitroguanidine, and other materials. Organic lead salts cause slightly high results if not removed, and barium chromate causes very high results.

A sintered porcelain crucible of fine porosity containing an asbestos pad is used for the filtration. A Gooch crucible is not satisfactory since it will not retain Channel Black completely. The filter crucible containing the pad must be ignited at 800° for 40 min before use, in order to remove organic matter in the asbestos that would react with nitric acid.

The results obtained for Channel Black in two propellants (Table I) showed satisfactory precision. The recoveries from synthetic samples prepared with 5 different Channel Blacks (Table II) were also satisfactory.

TABLE I.—RESULTS FOR CHANNEL BLACK IN TWO PROPELLANTS

Sample	Channel Black found, %	Average, %	Standard deviation, %
1*	0 20		
	0·19	0 20	0·015
	0·21		
	0 18		
	0 20		
2†	0 10		
	0 09		
	0 11	0 10	0·010
	0·11		
	0 09		

* Contains: 92·7% nitrocellulose, 5 7% dinitrotoluene, 0 65% diphenylamine.

† Contains: 87·9% nitrocellulose, 0 94% dinitrotoluene, 0 88% potassium sulfate, 0 75% tin.

TABLE II.—RESULTS FOR CHANNEL BLACK IN SYNTHETIC SAMPLES

Synthetic sample		
Matrix	Channel Black, %	Channel Black found, %
5 g IMR*	+0 06 Carbolac 1	0 05
5 g IMR*	+0·05 Royal Spectra	0·07
5 g DB†	+0 10 Spheron 6	0·10
5 g Sn — 1 ‡	+0 14 Monarch 74	0·15
5 g IMR*	+0 20 Carbolac 1	0 19
5 g DB†	+0 18 Carbolac 2	0·20
5 g IMR*	+0 20 Royal Spectra	0 19
5 g Sn — 1 ‡	+0 31 Spheron 6	0 33
5 g IMR*	+0 49 Monarch 74	0 47
5 g IMR*	+0 50 Carbolac 2	0 47
5 g IMR* + 0 25 g lead stearate	+0 20 Carbolac 1	0 22
5 g IMR* + 0 25 g lead stearate	+0 15 Royal Spectra	0 14
5 g IMR* + 0 25 g lead chromate	+0·22 Carbolac 1	0 20
5 g IMR* + 0 25 g lead chromate	+0 10 Spheron 6	0 10
5 g IMR* + 2 g nitroguanidine	+0 27 Monarch 74	0·25
5 g IMR* + 2 g nitroguanidine	+0 11 Spheron 6	0 11

* Contains: 90 3% nitrocellulose, 8 0% dinitrotoluene, 0 7% diphenylamine, 1 0% potassium sulfate, 0 19% graphite.

† Contains: 76 7% nitrocellulose, 19 42% nitroglycerin, 1 53% ethyl centralite, 1·45% calcium carbonate, 0 92 potassium nitrate, 0·15% graphite.

‡ Contains: 92 9% nitrocellulose, 5·55% dinitrotoluene, 0 79% diphenylamine, 0 76% potassium sulfate, 0·23% graphite.

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Summary—A spectrophotometric method is proposed for the determination of Channel Black in small arms propellants. The Channel Black is separated from the nitrocellulose and other organic compounds by dissolution of the propellant in morpholine and filtration through a sintered porcelain crucible containing an asbestos mat. The Channel Black is then dissolved by treating the mat and crucible with boiling nitric acid for 3 hr, the solution is filtered, and the yellow colour is measured The colour is due to polycarboxylic acids with cyclic nuclei. The range of the method is from 0 to 0 5% of Channel Black.

Résumé—On propose une méthode spectrophotométrique de dosage du noir de charbon dans les poudres propulsives des armes portatives. On sépare le noir de charbon de la nitrocellulose et autres composés organiques par dissolution de la poudre dans la morpholine et filtration à travers un creuset en porcelaine frittée contenant une couche d'amiante Le noir de charbon est alors dissous par traitement de la couche d'amiante et du creuset à l'acide nitrique bouillant pendant 3 h, la solution est filtrée et l'on mesure la coloration jaune. La coloration est dûe à des acides polycarboxyliques à noyaux cycliques. La méthode est utilisable pour des teneurs en noir de charbon allant de 0 à 0,5%.

Zusammenfassung—Eine spektrophotometrische Methode zur Bestimmung von Kanalruß in Handfeuerwaffen-Munition wird vorgeschlagen Der Kanalruß wird von der Nirtocellulose und anderen organischen Verbindungen durch Losen des Sprengstoffs in Morpholin und Filtration durch einen Porzellanfiltertiegel mit Asbestschicht getrennt. Der Kanalruß wird dann durch dreistundige Behandlung von Asbestschicht und Tiegel mit kochender Salpetersaure gelost, die Losung filtriert und die gelbe Farbung gemessen. Die Farbe kommt von cyclischen Polycarbonsauren. Die Methode funktioniert von 0 bis 0,5% Kanalruß.

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Synthetic and analytical studies on colour reagents—IX

The reactions of phthaleinazo compounds with the alkaline earths

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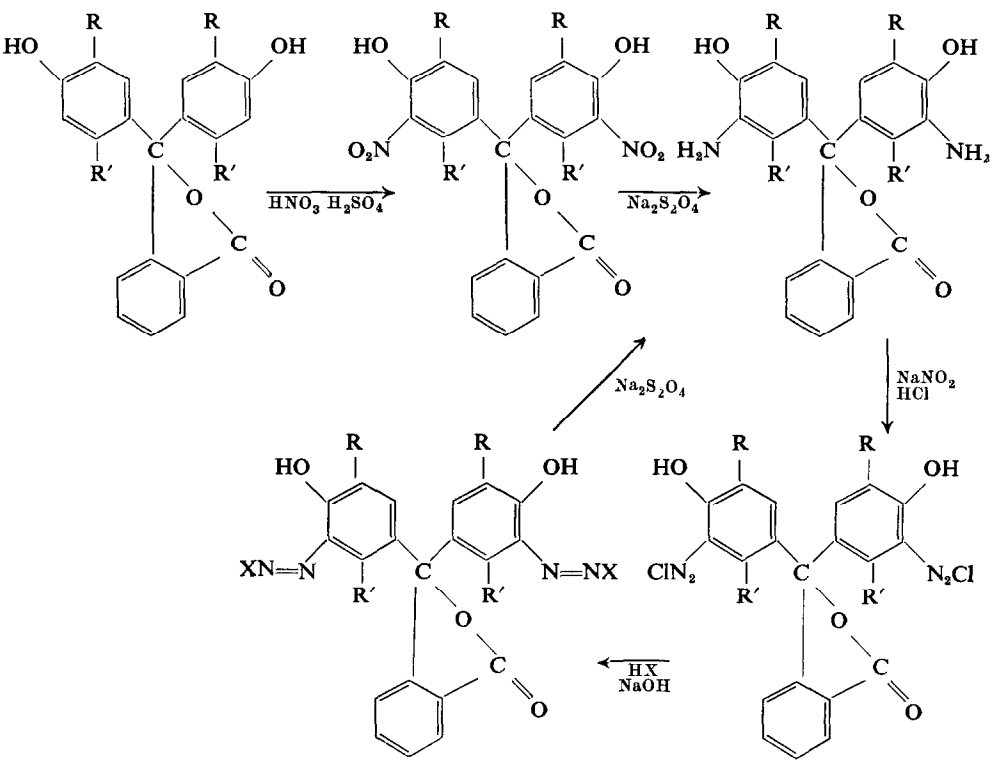
IT IS well known that *o,o'*-dihydroxyazo compounds react with the alkaline earths to form stable coloured chelates in alkaline media. To find more sensitive reagents for these elements, a series of phthaleinazo compounds was synthesized, and the limiting concentrations for the detection of magnesium, calcium, strontium and barium were determined.

EXPERIMENTAL

Synthesis of reagents

Phenolphthalein, Cresolphthalein, Thymolphthalein, Phenol Red, Cresol Red and Thymol Blue were used as starting materials and the syntheses were carried out as follows:



Sulphonphthalein derivatives were also synthesized in the same manner, except for nitration.

Nitration. Phthaleins were nitrated by Gatterman's method[1] (Cresolphthalein can also be nitrated by Bayer's method[2]). As sulphonphthaleins cannot be nitrated by Demont's method[3] the following procedure was used. The sulphonphthalein was dissolved in concentrated sulphuric acid, cooled to 0°, and the calculated amount of potassium nitrate, dissolved in concentrated sulphuric acid, was added dropwise

Reduction. The theoretical amount of sodium hydrosulphite was added little by little to the dinitro compound in alkaline solution. The colour of the solution turned from orange through green to blue.

The blue colour indicated the completion of the reaction. The blue solution was acidified with hydrochloric acid and filtered to remove unreacted dinitro compound. The filtrate was neutralized with ammonia solution to precipitate the diamino compound.

Diazotization and coupling. The diamino compound was dissolved in concentrated hydrochloric acid below 0°, and concentrated sodium nitrite solution was added dropwise. Diazotization of the two amino groups was judged to be complete from the amount of nitrite consumed. As the diamino derivatives of sulphonphthaleins are unstable, the compounds could not be prepared in the pure solid state, and the solution obtained by the reduction was directly diazotized without any purification The diazotized solution was added dropwise into a strongly alkaline solution containing chromotropic acid, R-acid, or 2-hydroxy-3-naphthoic acid, below 0°. After standing overnight at room temperature, the solution was acidified with concentrated hydrochloric acid to precipitate the phthaleinazo compound. (If the product is not precipitated, it may be salted out, or used directly in the solution as it is)

Determination of limiting concentrations

Magnesium, calcium, strontium and barium solutions were prepared from magnesium nitrate, calcium chloride, strontium nitrate and barium chloride, respectively. The concentrations were 0 1 μg/ml for magnesium and calcium and 1·0 μg/ml for strontium and barium. Various pH buffer solutions were prepared from ammonia solution, ammonium chloride and sodium hydroxide, in the range pH 8 5–13 5.

TABLE I.—DETECTION LIMITS FOR ALKALINE EARTHS (μg/ml) AT pH 11 3

Bis-diazo component	Coupling component	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Note
Phenol-phthalein	Chromotropic acid	0·0003	0 001	0·05	0 05	
	R-acid	0 001	0 005	0 05	0 05	
	2-Hydroxy-3-naphthoic acid	0 001	0 05	0 05	0 08	pH = 13 5, acetone
Cresol-phthalein	Chromotropic acid	0 002	0 002	0 3	0 1	
	R-acid	0·001	0·005	0·3	0 1	
	2-Hydroxy-3-naphthoic acid	0 001	0 01	0 3	0 06	pH = 12·5, acetone
Phenol Red	Chromotropic acid	0 001	0 03	0 05	0 1	
	R-acid	0 002	0 05	0 5	0 3	
	2-Hydroxy-3-naphthoic acid	0 001	0 03	0 1	0 1	pH = 12·5, acetone
Cresol Red	Chromotropic acid	0·001	0 05	1	0 8	
	R-acid	0 002	0 08	1	1	
	2-Hydroxy-3-naphthoic acid	0·001	0·05	0 2	0 1	pH = 12 5
Thymol Blue	Chromotropic acid	0 001	0 1	2	0 5	
	R-acid	0 001	0 1	0 5	0 5	
	2-Hydroxy-3-naphthoic acid	0 0003	0 05	1	0 3	pH = 12 5
Plasmocorinth B		0 001	0 03	0 1	0 1	
Eriochrome Black T		0 001	0 05	1	0 5	

Four ml of a solution of suitable pH were taken in a test-tube, and a small amount of the reagent solution was added to develop the colour. If the colour was already red, due to the presence of alkaline earths as impurities in the buffer solution, the colour change was reversed by the addition of just sufficient $2 \times 10^{-4}M$ EDTA solution to mask the impurities. The solution was divided between two test-tubes, and a few drops of the alkaline earth solution were added to one, and the colour was compared with the original. At the most favourable pH (at which the colour-change from blue to red is most distinct) a suitably diluted solution of the metal ion was added drop by drop and the minimum number of drops (at least one drop) after which the colour change was just noticeable, was determined. From the number of drops the limiting concentration was calculated. The results are summarized in Table I, along with those for Eriochrome Black T and Plasmocorinth B, because they are said to be very sensitive reagents for magnesium and calcium.

DISCUSSION

From Table I, the order of decreasing sensitivity of the cations is seen to be magnesium, calcium, strontium, barium, and the sensitivity is about the same as or better than that with Plasmocorinth B and Eriochrome Black T.

The substituents of the phthalein or sulphonphthalein have little effect on the limiting concentration for the detection of the metals, but the nature of the coupling component is much more important. As a coupling component, in *o*-hydroxyazo compounds, chromotropic acid, R-acid and 2-hydroxy-3-naphthoic acid are superior to the other components used.[4-6] The limiting concentrations for these reagents are not very different from each other.

Sulphonphthalein derivatives are very soluble in water, but the syntheses are difficult, and the pure compounds are not obtainable. From a consideration of the sharp-colour change and ease of synthesis, bis (chromotropeazo)phenolphthalein is the best one.

2-Hydroxy-3-naphthoic acid derivatives differ from chromotropic acid and R-acid derivatives. The latter are blue at pH 10–13, but the former are red at pH 9·5–10 4 and blue at pH 11·3–13 5, but the chelates are blue at pH 9 5–10 4 and red at pH 11·3–13 5. At pH 10 4, the limiting concentration is 0 002 μg/ml for magnesium, 0 1 μg/ml for calcium, and 0 5 μg/ml for strontium and for barium, and these values are somewhat higher than those in Table I The addition of acetone improves the sensitivity of these reagents

Bis(chromotropeazo)phenolphthalein was found to react with thorium at pH 2, and the limiting concentration was 10 μg/ml. This compound is the most sensitive reagent for alkaline earths yet found, its higher sensitivity probably being due to its being an *o,o'*-dihydroxyazo compound, and having a larger conjugated system than a monoazo compound, and also due to the ease with which the human eye differentiates red from blue.

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Summary—Some new phthaleinazo compounds—*o,o'*-dihydroxyazo compounds—have been prepared by coupling chromotropic acid, R-acid, and 2-hydroxy-3-naphthoic acid with bis-diazotized diaminophthaleins. These compounds have been found to be very sensitive colour reagents for alkaline earths in alkaline media, and in particular, bis(chromotropeazo)phenolphthalein is the most sensitive yet found.

Zusammenfassung—Einige neue Phthaleinazoverbindungen—*o,o'*-Dihydroxyazoverbindungen—wurden durch Kupplung von Chromotropsaure, R-Saure und 2-Hydroxy-3-naphthoesaure mit tetrazotierten Diaminophthaleinen dargestellt. Diese Verbindungen stellen sehr empfindliche Farbreagentien auf Erdalkalien in alkalischen Medien dar; insbesondere ist Bis(chromotropazo)phenolphthalein das empfindlichste unter den bisher bekannten Reagentien.

Résumé—On a préparé quelques nouveaux composés phtaléinazo—*o,o'*-dihydroxyazo composés—par copulation de l'acide chromotropique, de l'acide R et de l'acide 2-hydroxy 3-naphtoique avec des diaminophtaléines bis-diazotées. On a trouvé que ces composés sont des réactifs colorés très sensibles des alcalino-terreux en milieu alcalin et, en particulier, la bis (chromotropeazo) phénolphtaléine est le plus sensible trouvé jusqu'à présent.

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PRELIMINARY COMMUNICATION

New method for the determination of pentachlorophenol by atomic absorption spectrophotometry

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IN atomic absorption spectrophotometry, a hollow-cathode lamp which emits the spectral lines belonging to the element being determined is generally used as a light source. Because of this restriction, it has been impossible to determine organic compounds directly by atomic absorption methods.

In the course of studies on solvent extraction with cationic metal chelate[1] it was found that the anions of pentachlorophenol (PCP) could be extracted into nitrobenzene if the aqueous solution contained an excess of tris(1,10-phenanthroline)iron(II) cations, and that it was possible to determine a small amount of PCP by measuring the absorbance of the extracts spectrophotometrically. By continuous variation methods the chemical formula of the extracted species was deduced to be $[Fe(phen)_3]$ $(C_6Cl_5O)_2$.

It also appeared possible to determine the PCP by spraying the extracted nitrobenzene solution into the flame of an atomic absorption spectrophotometer with an iron hollow-cathode lamp as a light source.

The recommended procedure for obtaining the calibration curve is as follows.

Mix 5 ml of tris(1,10-phenanthroline) iron(II) sulphate solution ($2 \times 10^{-2}M$), 10 ml of $0{\cdot}3M$ phosphate buffer solution (pH 7), and varying amounts of standard PCP solution ($1{\cdot}25 \times 10^{-3}M$ 0–6 ml). Dilute the solution with water to 25 ml and shake it for 3 min with 10 0 ml of nitrobenzene. Separate the organic phase and dry it with 1 g of anhydrous sodium sulphate. Measure the atomic absorption at the 2483 Å iron line. (A Nippon Jarrell-Ash atomic absorption spectrophotometer Model AA-1 equipped with an iron hollow-cathode lamp was used in our work, together with an air–acetylene flame from a 10-cm slit burner used with an air flow-rate of 6 0 l/min and an acetylene flow-rate of 1·2 l/min.)

Under these conditions, the calibration curve was found to be linear for the range tested ($0–3 \times 10^{-4}M$) of PCP concentration in aqueous solution.

The effect of other ions is probably the same as that in the spectrophotometric method.[1]

Although several methods have recently been reported,[2–4] the method proposed here has a higher sensitivity.

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Summary—A new application of atomic absorption is reported for the determination of pentachlorophenol. The method is based on solvent extraction into nitrobenzene of the ion-pair formed between tris(1,10-phenanthroline)iron(II) and the anion of pentachlorophenol, and the subsequent determination of the iron concentration in the extract by atomic absorption at the 2483 Å iron line.

Zusammenfassung—Es wird uber eine neue Anwendung der Atomabsorption zur Bestimmung von Pentachlorphenol berichtet. Die Methode beruht auf der Extraktion des Ionenpaars aus Tris(1,10-phenanthrolin)-eisen(II) und dem Anion von Pentachlorphenol in Nitrobenzol und nachfolgender Bestimmung der Eisenkonzentration im Extrakt durch Atomabsorption in der Eisenlinie bei 2483 Å.

Résumé—On rapporte une nouvelle application de l'absorption atomique pour le dosage du pentachlorophénol. La méthode est basée sur l'extraction par solvant en nitrobenzène de la paire ionique formée entre la tris(1,10-phénanthroline)fer(II) et l'anion du pentachlorophénol, et la détermination subséquente de la concentration en fer de l'extrait par absorption atomique à la raie 2483 Å du fer.

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TALANTA REVIEW

PRESENT STATE OF COMPLEXOMETRY—III*†

DETERMINATION OF UNIVALENT METALS

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Summary—A review of the visual complexometric determination of univalent metals is presented. Because of the low complex-forming tendency, all methods are based on indirect determinations such as displacement reactions or precipitation of the univalent metal in a form which can be determined complexometrically.

GENERALLY speaking, the univalent cations of silver, mercury, thallium and the alkali metals are not suitable for complexometry, because they have very little tendency to form complexes with EDTA or other titrants. The strongest of their EDTA complexes are those of silver ($\log K_{AgY} = 7{\cdot}2$) and probably of thallium(I). For silver there are already enough methods for its volumetric determination. For thallium we prefer its complexometric determination as the tervalent cation.[1] For alkali metals, only indirect methods can be used, based generally on the isolation of the elements as insoluble double salts with other metals which can be determined complexometrically. Such methods are time-consuming and require careful control of the experimental conditions, especially if they are carried out on the micro scale. On the other hand the great importance of sodium and potassium in biological fluids (blood, serum, erythrocytes, urine, *etc.*) has brought about a considerable interest in these methods. If we take into account, for example, the difficulties in the determination of sodium or potassium in biological material we have to appreciate that even here complexometry has contributed much towards simplifying and speeding up clinical routine work.

SILVER
($\log K_{AgY} = 7{\cdot}2$)[2]

If we add EDTA solution drop by drop to silver nitrate solution a white precipitate of the silver salt appears and redissolves in excess of EDTA, forming a complex AgY^{3-}. The silver-EDTA complex is very weak and reacts with all the important reagents for silver even if EDTA is present in large excess. This is very useful not only for qualitative tests but also for gravimetric, titrimetric and colorimetric determinations

* For reprints of this review see the Advertizement on the facing page.
† Part II, *Talanta*, 1966, **13**, 1223.

with various organic reagents such as dithizone, mercaptophenylthiazole, mercaptophenylthiodiazolone, benztriazole *etc*,[3] because many interfering elements can be masked with EDTA.

Direct determination. Only two methods for the direct visual determination of silver have been published. Belcher[4] recommended *o*-cresolphthalein-complexone (Metalphthalein) as indicator. Klein and Skřivánek[5] more recently determined silver, using Thymolphthalexone as indicator. A number of metals interfere, so the methods can be used only for pure silver solutions.

Štráfelda[6] has described the potentiometric determination of silver with the use of a silver indicating electrode. The method has the same limitation as those mentioned above.

Indirect determination. Flaschka and Huditz[7] developed a method based on a displacement reaction:

$$Ni(CN)_4^{2-} + 2\,Ag^+ = 2\,Ag(CN)_2^{2-} + Ni^{2+}. \qquad (1)$$

The nickel is determined in ammonia solution with EDTA and Murexide as indicator. Despite the unfavourable equivalent (2 Ag ≡ Ni) the method gives accurate results, according to the authors, and can be used on the micro scale not only for silver but also for its insoluble salts (AgCl, AgBr, AgCNS, *etc.*) and hence for the indirect determination of halogens.[8] Gedansky and Gordon[9] used this method for milligram quantities of silver, detecting the end-point photometrically.

Another method is the so-called amalgam method. Silver reacts with various amalgams (zinc, cadmium) and the displaced metal is determined complexometrically.[10,11] This method is mainly of theoretical interest.

Small amounts of silver can be determined by the displacement reaction between silver ion and copper diethyldithiocarbamate (DDC) dissolved in carbon tetrachloride or chloroform:

$$Cu(DDC)_2 + 2Ag^+ = 2AgDDC + Cu^{2+}. \qquad (2)$$

The copper is then determined complexometrically in slightly acidic medium. This method is more selective but also suffers from an unfavourable equivalent.[12]

Interferences. As already mentioned, almost all elements interfere to such an extent that separation of the silver or its determination by another method is necessary.

Separation and masking. In many cases silver is separated automatically during the decomposition of the sample, *e.g.*, by dissolution of alloys *etc.* with nitric and hydrochloric acid. Silver does not usually interfere in the determination of other metals provided that it does not react with the indicator. In special cases it can be masked with potassium cyanide.

Practical applications. Flaschka's method has been used by Amin[13] for the determination of silver in coinage and in photographical materials.[14]

MERCURY(I)

Mercury(I) disproportionates after addition of EDTA, according to the equation:

$$Hg_2^{2+} + H_2Y^{2-} = Hg + HgY^{2-} + 2H^+. \qquad (3)$$

This reaction has been recommended instead of that with ammonia, for the microdetection of mercury(I).[15]

THALLIUM(I)

Direct determination. Only one method for thallium(I) has been published, by Foley and Pottie.[16] They followed the titration spectrophotometrically at 222 mμ, using an ammonia-ammonium chloride buffer at pH 10.

Indirect determination. Sen[17] isolated thallium(I) as insoluble $Tl_2Ag[Co(NO_2)_6]$ and after dissolution of the precipitate in nitric acid he determined the cobalt complexometrically in acetone medium with thiocyanate as indicator. The method suffers from the unfavourable equivalent and has not been applied.

LITHIUM

($\log K_{LiY} = 2{\cdot}79$)

Only indirect methods for lithium are known. De Sousa[18] precipitated the chloride of lithium chloride with silver nitrate and dissolved the silver chloride after filtration, in potassium nickel cyanide according to equation (1) and determined the nickel by EDTA titration. His method was applied to the micro-determination of 50–500 μg of lithium oxide with an error of 0·5%. Previous separation from potassium and sodium is necessary, so that this method gives no improvement on other methods for lithium.

SODIUM

($\log K_{NaY} = 1{\cdot}66$)

All methods for sodium determination are based on its isolation as a triple salt of the composition $NaMe(UO_2)_3(CH_3CO_2)_9$ where Me is a bivalent metal. The metal Me is then determined complexometrically. Flaschka[19] was the first to propose the precipitation of sodium with zinc uranyl acetate and the determination of zinc with EDTA in ammonia buffer, Eriochrome Black T being used as indicator. The uranyl ion was masked with ammonium carbonate. The same method was published five years later by Sen[20] without citation of Flaschka's paper. Holasek and Duganžić[21] improved Flaschka's method, using dithizone as the indicator for zinc, which gives a sharp end-point even in titrations with 0·001*M* EDTA.

Gagliardi and Reimers[22] have studied thoroughly other metallic acetates as reagents for sodium precipitation. According to these authors nickel and cobalt uranyl acetates are the best precipitants for the gravimetric or complexometric determination of sodium. Doležal *et al.*[23] have found magnesium uranyl acetate and cobalt uranyl acetate the best for the precipitation of sodium. They determine the uranium complexometrically after its reduction with ascorbic acid, *e.g.*, by back-titration with 0·01*M* thorium nitrate, using Xylenol Orange as indicator. Their attempts to determine both the uranium and the cobalt together (to the equivalent) were unsuccessful.

Gagliardi and Reimers[24] have also published an interesting method for sodium determination (together with potassium) based on ion-exchange with Lewatit S 100 in the magnesium form. The exchanged magnesium is determined complexometrically. In another portion of the eluate, potassium is determined by precipitation with sodium tetraphenylborate.

Interferences. According to Gagliardi and Reimers[22] sodium can be determined by precipitation as triple acetate in the presence of a large excess of calcium, magnesium, barium, manganese, cobalt, cadmium, copper, zinc and iron(II). Potassium

does not interfere when present up to a ratio of K:Na = 1·5:1. Doležal *et al.*[23] found that the precipitation of sodium with cobalt uranyl acetate is not affected by the presence of ammonium, zinc, magnesium, iron(II), calcium, strontium, barium and mercury. Lithium is coprecipitated, and potassium in an amount twice that of the sodium makes the results high.

Practical applications. Sodium has been determined in blood serum,[25] in glass,[26] in mineral waters[23] and in some pharmaceuticals such as *natrium citricum*, *natrium salicylicum* and *natrium gentisicum*.[23]

POTASSIUM

For potassium also, only indirect complexometric methods have been described, based on the isolation of slightly soluble compounds of the type $K_2Me[Co(NO_2)_6]$. The first method was introduced by Flaschka and Holasek[27] who precipitated potassium as $K_2Na[Co(NO_2)_6]$. After dissolution of the isolated precipitate in hydrochloric acid and destruction of nitrous oxides with urea, they determined the cobalt in slightly ammoniacal solution with EDTA, using Murexide as indicator. In slightly acid medium cobalt can be determined directly with the Cu-EDTA-PAN system.[28] Indirect determination by back-titration with zinc and Eriochrome Black T[29,30] can also be used under the proper conditions. The method has the same disadvantages as the classical gravimetric method—the solubility of the precipitate, and variation in the composition of the precipitate and hence in the Co:K ratio.

The same principle has been studied by Taketatsu[31] and Soibelman.[32] Sen[17] isolated potassium as the silver salt $K_2Ag[Co(NO_2)_6]$ and determined the cobalt with EDTA, using ammonium thiocyanate as indicator.

De Sousa[33] precipitated potassium as perchlorate, separated it, reduced the perchlorate to chloride, precipitated this as silver chloride, and determined silver according to reaction (1). His method is tedious and does not seem very useful.

A very promising method was proposed by Flaschka and Sadek[36] and by Sadek and Reilley.[37] The well-known reagent sodium tetraphenylborate precipitates potassium quantitatively as $K(C_6H_5)_4B$ and can be used for the gravimetric and titrimetric determination of potassium. The authors mentioned have found that the isolated potassium salt (dissolved in organic solvents) reacts with the mercury-EDTA complex and forms a white precipitate of a phenylmercury salt. The reaction proceeds according to the equation:

$$4HgY^{2-} + (C_2H_5)_4B^- + 8H_2O = H_3BO_3 + 4C_6H_5Hg^+ + 4H_2Y^{2-} + 5OH^-. \quad (4)$$

The liberated EDTA is determined complexometrically and has a very favourable conversion factor (1 mole of K corresponds to 4 moles of EDTA).

Flaschka dissolved the isolated $K(C_6H_5)_4B$ in acetone, added an excess of mercury-EDTA and back-titrated with zinc solution, using PAN indicator. Reilley[37] has found that fair results could be obtained by titrating the liberated EDTA with lead solution, using Xylenol Orange as indicator. Another modification has been proposed by Reilley[37] based on the dissolution of the potassium salt in dimethylformamide and, after addition of mercury-EDTA solution, titration of the freed EDTA with magnesium solution at pH 10, with Eriochrome Black T as indicator. The same procedure has been recommended by the author for the determination of ammonium ions. Gagliardi

and Reimers[24] have also used the tetraphenylborate method (see section on *Sodium*, above).

Interferences. The simple precipitation of potassium as a double salt cannot be carried out in the presence of ammonium, rubidium, caesium or thallium(I). The presence of other metals also interferes so that the determination of potassium is possible only in pure solutions of it or in those cases where those a condition can be simply achieved, in the analysis of blood serum for example.

Elimination of interferences. Pécar[34] studied thoroughly the influence of ammonium ions on the precipitation of potassium on the micro scale. He proposed the oxidation of ammonia with hypobromite in sodium hydroxide solution. The method has one disadvantage—sodium hydroxide always contains potassium (*e.g.*, reagent grade sodium hydroxide contains up to 0·09% of potassium) and the blank is too high for microanalysis. He recommended, together with Holasek and Lieb,[35] the masking of ammonia with formaldehyde. The method works well up to 0·02*M* concentration of ammonia and can probably be applied for the analysis of blood, urine and other biological fluids.

Practical applications. Complexometric determination of potassium has value only in the analysis of various biological materials such as blood serum, urine, *etc.*[27,28,30,34,38]

RUBIDIUM AND CAESIUM

Complexometric methods for rubidium and caesium are similar to those for potassium. Sen[17] proposed precipitation of both as $Me_2Ag[Co(NO_2)_6]\cdot H_2O$ and direct determination of the cobalt after the dissolution of the precipitate. Cygański[39] precipitated caesium as $Cs_3[Co(NO_2)_6]\cdot H_2O$, and Ciogolea[40] isolated caesium as $CsBiI_4$ and determined the bismuth complexometrically. De Sousa[41] precipitated caesium as perchlorate and converted it into chloride, which he precipitated as silver chloride. The silver was then determined according to Flaschka's method.[7]

Zusammenfassung—Es wird eine Übersicht über die visuelle komplexometrische Bestimmung einwertiger Metalle gegeben. Wegen der geringen Komplexbildungstendenz beruhen alle Methoden auf indirekten Bestimmungen wie Verdrängungsreaktionen oder Fällung des einwertigen Metalls in einer komplexometrisch bestimmbaren Form.

Résumé—On présente une revue sur le dosage complexométrique visuel des métaux monovalents. Par suite de la faible tendance à former des complexes, toutes les méthodes sont basées sur des déterminations indirectes telles que des réactions de déplacement ou la précipitation du métal monovalent sous une forme qu'on peut doser par complexométrie.

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TALANTA REVIEW

PRESENT STATE OF COMPLEXOMETRY—IV*†
DETERMINATION OF RARE EARTHS

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Summary—A review of the visual complexometric determination of the rare earths, scandium and yttrium with various volumetric reagents is presented. As in previous parts attention is paid to the complexometric behaviour of these metals and to the problems of interferences in their determinations. Methods for the determination of thorium, scandium and some rare earths in mixtures are described in detail. Recent developments and further possibilities in this field are discussed.

ACCORDING to Vickery, scandium and yttrium should be included in the family of rare earths as members of the IIIA group because their electronic 5*d* shell is also empty or incomplete. In addition, they usually accompany the lanthanides in natural sources such as monazite sand.

The expression "rare" does not mean that rare earths are scarcely to be found, but relates to their concentration, which is usually very low in minerals. The amount of rare earths liberated by dissolution of Florida apatite for phosphoric acid production is estimated, according to *Chemical News* (October 1966), at about 3500 tons. The price of some rare earths is still very high: 1 lb of europium costs about $1500 and 1 lb of thulium $2–4000.

Industrial use of rare earth metals and oxides is increasing, especially in electronics. For example, europium is in demand for activation of yttrium vanadate, used as a red phosphor in TV tubes, and samarium and praseodymium compounds are used as cracking catalysts in the petroleum industry. Another potential application of rare earth metals is in the processing of magnesium alloys and high-melting metals. Rare earths are very important for the production of special glasses and ceramics, and their semiconductor and superconductor properties have found wide practical utilization. Some rare earths play an important part in the development of garnets for radio masers, and have many applications in nuclear chemistry.

The complexometry of the rare earths represents only a very small part of the chemistry of rare earth complexes with polyaminopolycarboxylic acids. Great attention has been paid to the chemical and physico-chemical properties of these rare earth complexes, especially their stability constants which are important not only for complexometric determination, but also for chromatographic ion-exchange separations. The high purity of individual rare earths now on the market has been achieved

* For reprints of this Review see the Advertizement near the front of this issue.
† Part III, *Talanta*, 1967, **14**, 613.

by means of chromatography, with nitrilotriacetic acid (NTA), ethylenediaminetera-acetic acid (EDTA), or similar complex-forming compounds as eluents. It is probable that the details of these large-scale separations and purifications are kept secret, or are only partly published.

The stability constants of rare earth complexes with the most important poly-aminopolycarboxylic acids are summarized in Table I.

COMPLEXOMETRY OF THE RARE EARTHS (RE)

The volumetric determination of the rare earths was practically unknown before EDTA and related compounds were introduced in analytical chemistry. The application of EDTA and other titrants such as 1,2-diaminocyclohexanetetra-acetic acid

TABLE I.—STABILITY CONSTANTS FOR METAL COMPLEXES OF SOME POLYAMINOPOLYCARBOXYLIC ACIDS

	log K_{My}								
	IMDA	HIMDA	NTA	EDTA	HEDTA	EGTA	DTPA	DCTA	PDTA
La	5·88	8·00	10·37	15·50	13·82	15·55	19·43	16·26	16·42
Ce	6·18	8·46	10·83	15·98	14·45	15·70	20·50	16·76	16·79
Pr	6·44	8·64	11·07	16·40	14·96	16·05	21·07	17·31	17·17
Nd	6·50	8·80	11·25	16·61	15·16	16·28	21·60	17·68	17·54
Sm	6·64	9·10	11·51	17·14	15·64	16·88	22·34	18·38	17·97
Eu	6·73	9·10	11·49	17·35	15·62	17·10	22·39	18·62	18·26
Gd	6·68	9·01	11·54	17·37	15·44	16·94	22·46	18·77	18·21
Tb	6·78	9·08	11·58	17·90	15·55	17·27	22·71	19·50	18·64
Dy	6·88	9·08	11·71	18·30	15·51	17·42	22·82	19·69	19·05
Ho	6·97	9·14	11·85	18·74	15·55	17·38	22·78	—	19·30
Er	7·09	9·24	12·00	18·85	15·61	17·40	22·74	20·68	19·61
Tm	7·22	9·35	12·20	19·32	16·00	17·48	22·72	20·96	20·08
Yb	7·42	9·38	12·37	19·51	16·17	17·78	22·62	21·12	20·25
Lu	7·61	9·50	12·47	19·83	16·25	17·81	22·44	21·51	20·56
Y		9·22	11·40	18·10				19·15	18·78
Sc				23·10					
Th				23·20			27·00	23·20	

IMDA = Iminodiacetic acid; HIMDA = *N*-Hydroxyethyliminodiacetic acid;
NTA = Nitrilotriacetic acid; EDTA = Ethylenediaminetetra-acetic acid;
HEDTA = *N*-Hydroxyethylethylenediaminetriacetic acid;
EGTA = Ethyleneglycol-bis(2-aminoethylether)tetra-acetic acid;
DTPA = Diethylenetriaminepenta-acetic acid;
DCTA = 1,2-Diaminocyclohexanetetra-acetic acid;
PDTA = Propylenediaminetetra-acetic acid.

(DCTA), triethylenetetraminehexa-acetic acid (TTHA) and diethylenetriaminepenta-acetic acid (DTPA) brought valuable progress in the analytical chemistry of the rare earths. Even so, the chemical similarity of these elements allows accurate determination to be made only of the sum of the rare earths present or of individual ones already isolated from the others, and the analysis of their mixtures by complexometry only is impossible, with the exception of some attempts which will be described later.

Direct determinations. The first determination of rare earths was described by Flaschka.[1] He titrated them in alkaline medium at pH 8–9 with tartaric or citric acid present to prevent hydrolysis. Eriochrome Black T was used as indicator and the titration had to be performed on boiling solutions. The pH is critical, as

above pH 9 the RE-complexes with the indicator are too stable and do not react with EDTA. Flaschka described the determination of milligram amounts of yttrium, samarium, praseodymium and gadolinium. Chromazurol S as indicator for RE was proposed by Malát and Tenorová.[2] This indicator works in pyridine medium.

The stability constants of the RE-EDTA complexes are high enough for RE determination in acidic medium, for which carminic acid,[3] Brompyrogallol Red,[4] Galleine,[5] Azoxin S,[6] and Eriochrome Black T in urotropine medium[7] have been proposed as indicators. Azoarsonic acids (Arsenazo) have been thoroughly studied as indicators for these rare earth titrations.[8–10] The most important indicators for complexometry may be considered to be Xylenol Orange[11,12] and Methylthymol Blue.[13] The reaction of both indicators is very sensitive and therefore they have also been proposed as colorimetric reagents for a great number of metals, including the rare earths. Xylenol Orange has been used by Kinnunen and Wennestrand for the titration of RE.[14]

Indirect determinations. Back-titration of excess of EDTA can be performed in many ways. Such methods are most useful when difficulties in the direct titration are expected, *e.g.*, if RE and oxalates or phosphates are present together, or some metallic impurities are there which have to be masked. Only the back-titration at pH 5–6 with zinc, and Xylenol Orange as indicator, is worth mentioning.

Other volumetric reagents for RE. Under the same experimental conditions as for EDTA, RE can be determined with DCTA, DTPA and TTHA. Their advantages over EDTA in special cases will be mentioned further.

Interferences. All elements having log $K > 11$ for their EDTA complexes interfere or are co-titrated even in acidic solutions. Of anions, fluoride masks and phosphate precipitates all rare earths. Oxalate interferes only in direct titrations, because in acidic medium oxalates of the rare earths are also precipitated. Their ignition to the oxides is not necessary if we determine the RE indirectly. Misumi and Taketatsu[15] dissolve the isolated RE-oxalates in alkaline EDTA solution by warming to 60°, and titrate the excess of EDTA with magnesium sulphate solution, using Eriochrome Black T as indicator. According to the authors the pH of the titrated solution has to be correctly adjusted to 10·5. Their results have shown that the presence of 40–70 mg of oxalic acid obscures the end-point. For this reason the method is suitable only for microtitrations of rare earths (1–5 mg). A more reliable method is described by Lyle and Rahman,[16] based on the dissolution of the RE-oxalates in hydrochloric acid. After addition of an excess of EDTA, the pH is adjusted to 5–6 and the excess of EDTA is determined by zinc titration, with Xylenol Orange as indicator.

Elimination of interferences. Only a few possibilities exist for RE determination without previous masking or separation. The alkaline earths do not interfere with the determination of RE in acidic medium. On the other hand metals forming the most stable complexes with EDTA can be determined in the presence of rare earths. Successive determination of bismuth at pH 2 and neodymium or praseodymium at pH 5–6, Xylenol Orange being used as indicator, was described by Milner and Edwards.[17] The micro-determination first of scandium and then of rare earths was described by Hung Shui-Chieh and Liang Shu-Chuan,[18] who titrated 1–400 μg of scandium oxide in a small porcelain crucible at pH 1·8–2·2 with 0·05M EDTA after adding a small amount of Xylenol Orange. Consecutive microtitrations of scandium

and the rare earths are possible up to the ratio Sc_2O_3:Ln_2O_3 1:1000. Zirconium can be determined with EDTA in solutions of 0·4–0·6*M* nitric acid in the presence of all rare earths.[19]

Masking of metals. Some bivalent metals such as copper, zinc and cadmium are masked with potassium cyanide in Flaschka's method for the determination of RE.[1] In slightly acidic medium these cations are masked with 1,10-phenanthroline.[20] Thiourea can be used for selective masking of copper, and sulphosalicylic acid at pH 7–8 for masking of aluminium and iron.[9] According to these authors,[9] thorium is masked with sulphosalicylic acid at pH 5, but according to Chuan,[18] not at pH 2. Very small amounts of zirconium up to 50 μg are also masked with sulphosalicylic acid at pH 2.[18]

Masking and separation of rare earths. Only fluoride can be used for the masking of the rare earths even if they are present as EDTA-complexes. This allows for example the consecutive titration of heavy metals and iron by back-titration with zinc solution and Xylenol Orange. After determination of the total of all elements ammonium fluoride is added and the liberated EDTA is titrated with zinc solution.

For the separation of rare earths a number of methods have been proposed. Their precipitation as oxalates is the best known. Triethanolamine has been used as masking agent for iron, aluminium and bivalent metals in the precipitation of lanthanum with sodium hydroxide.[20] Various ion-exchange separation methods have also been described, but are outside the scope of this review.

Complexometry is not limited to the determination of rare earths in "pure solutions". There are many problems to be solved such as their determination in the presence of thorium, scandium, yttrium, uranium, titanium, phosphates, EDTA, and other complex-forming compounds and extraction reagents.

Determination of RE in the presence of phosphates

Phosphates interfere by forming insoluble phosphates under the conditions suitable for the complexometry of the rare earths. Usually ion-exchange is used for the separation of rare earths from phosphate. Even the indirect complexometric determination of RE with EDTA or DCTA is impossible because most of the rare earths are displaced from their complexes during the titration with the zinc solution, and precipitated again.[21] Recently we have found that only DTPA can be used for such determinations.[22] The RE-phosphates are dissolved in small volume and an excess of 0·05*M* DTPA is added with ascorbic acid or hydroxylamine hydrochloride, the pH is adjusted with ammonia and urotropine to 5–6 and the excess of DTPA is then titrated with zinc solution to the Xylenol Orange end-point. Scandium can be determined together with RE. Thorium interferes by forming an insoluble phosphate during the neutralization and dilution of the solution, even in the presence of DTPA.

Determination of RE in the presence of EDTA

Many chromatographic separation methods use either RE–EDTA complexes at various pH values or EDTA solutions of various pH values to elute individual rare earths or small groups of them from the column. In both cases, the eluate contains EDTA and one or more of its rare earth complexes, depending on the conditions of elution. Because ion-exchange techniques are used on the large scale, the determination of rare earths in EDTA solutions is very important.

Martynenko[23] proposed their precipitation, from one aliquot, as oxalates and determination as oxides. In a second aliquot he determined the free EDTA complexometrically. The total amount of EDTA present could then be calculated from the titration and from the amount of oxides found. A simpler method was described by Tereshin and Tananaev.[24] They determined all the EDTA at pH 2 with 0·04*M* iron(III) chloride, using sulphosalicylic acid as indicator. After adjusting the pH to 4·5–6 they determined all the rare earths with 0·04*M* EDTA, with Xylenol Orange as indicator. The relative error of a single determination by both procedures was ±0·7%.

Determination of RE in the presence of alkyl phosphates

Sheka and Sinyavskaya[25] have found that dialkyl hydrogen phosphates do not affect the direct titration of rare earths with 0·001*M* EDTA, Xylenol Orange being used as indicator. Yttrium in the presence of dibutylphosphate is determined by back-titration with lanthanum chloride. This method is useful after liquid-liquid extraction of small amounts of rare earths from other elements.

Determination of scandium or thorium and RE

The consecutive titration of scandium and the rare earths has been already mentioned.[18] Chernikov[26] applied the same method for the successive determination of thorium (at pH 1·2–2·5) and then the rare earths (at pH 5–6), using Xylenol Orange as indicator. According to this author the method is good up to the ratio Th:RE = 1:70, but we have never succeeded in reproducing his results. In acidic solution a neutral complex of thorium, ThY, is formed. Above pH 4, a ternary EDTA-Th-XO complex is formed, which makes further determination of rare earths impossible. Indeed, this red-violet complex exists in the presence of large amounts of EDTA or DCTA. This reaction has been used not only for the detection of thorium in the presence of scandium and rare earths[27] but also for the detection of EDTA in mixtures with other compounds (DTPA, TTHA)[28] as well as for the complexometric determination of DTPA or TTHA in the presence of EDTA.[29] This determination is carried out with thorium nitrate at pH 5–6, the titration solution being heated. The first traces of thorium added after the reaction with DTPA or TTHA is complete are bound with EDTA but then react with Xylenol Orange, giving a very good end-point. It is probable that not only a 1:1:1 complex (Th:XO:EDTA) is formed but also binuclear or more complicated complexes, as may be assumed from the existence of the $Th_2(XO)_2$ complex.[30] DCTA behaves similarly and cannot be used for the successive determination of thorium and rare earths.

DTPA and TTHA are most suitable for the titration of thorium plus RE. With both these titrants we determine thorium at pH 2·5–3·5 and then the rare earths in urotropine medium at pH 5–6, using Xylenol Orange as indicator.[31] The titration with DTPA has been used also for heavy RE by Gupta and Powell,[32] and the titration with TTHA by Mukherji.[33] Both titrations have been found reliable.

Peshkova and coworkers[34] recommended Arsenazo as indicator for the consecutive titration of thorium and rare earths, using photometric detection of the end-point, but Chernikov[18] did not succeed with the visual titration because of blocking of the Arsenazo with thorium.

Determination of thorium, scandium and light lanthanides

Successive determination of the sum (Th + Sc) and then the rare earths is possible with DTPA as described in the preceding paragraph. For the individual determination of thorium and scandium and rare earths another method has to be used. The thorium EDTA and DCTA complexes react with TTHA according to the equation:

$$\text{Th—DCTA} + \text{TTHA} = \text{Th—TTHA} + \text{DCTA}. \qquad (1)$$

This reaction is quantitative in hot solutions buffered with urotropine. The scandium DCTA and EDTA complexes do not react at all. The excess of TTHA and the liberated DCTA can be determined very easily by titration with zinc solution, with Xylenol Orange as indicator.[35] In the presence of rare earths, however, the situation is more complicated. The added TTHA reacts at pH 5–5·5 (urotropine buffer) with the free rare earths, forming 1:1 complexes. The DCTA liberated according to reaction (1) does not react with the TTHA complexes of lanthanum, cerium, praseodymium and neodymium, but the heavier rare earths are partly displaced:

$$\text{RE—TTHA} + \text{DCTA} = \text{RE—DCTA} + \text{TTHA}. \qquad (2)$$

The determination of thorium and scandium and the first four lanthanides can be carried out on two aliquots by differential back-titrations of excess of reagent with zinc and lanthanum, which form different types of complex with DCTA and TTHA.[36]

Analysis of rare earth mixtures

The simplicity of the complexometric titrations presents a great inducement to try to use them for the determination of rare earth mixtures. Consecutive titrations cannot be carried out, however, because the stability constants of the rare earth complexes are too close to each other. From the theoretical point of view the difference in the logarithm of the constants has to be at least 4–5 for consecutive titrations to be possible. Not even in the combination of the first and last members of the series (lanthanum and lutetium) is this condition fulfilled, and there is little hope of ever finding special masking agents for single rare earths or for small groups of them.

Some years ago Patrovský[37] utilized the difference in the atomic weights of yttrium (88·92) and erbium (167·27) for their determination in their mixtures. The oxalates were isolated, ignited, and weighed. The oxides were dissolved and their mixture titrated complexometrically with EDTA, Xylenol Orange being the indicator. If 0·02*M* EDTA is used the amount of the oxides present can be calculated according to the equations

$$\text{mg } Y_2O_3 = \frac{3{\cdot}824V - E}{0{\cdot}6935}; \quad \text{mg } Er_2O_3 = \frac{2{\cdot}582V - E}{0{\cdot}4094}$$

where V is the consumption of 0·02*M* EDTA in ml, and E is the weight of the isolated oxides. According to the author this method can also be used for the determination of yttrium and the sum of the yttrium earths if these are present in the sample in approximately equal amounts. The atomic weight of terbium (158·93) is compensated for by the atomic weight of lutetium (174·99) giving the value 166·96 which is close

to the atomic weight of erbium. The author used this procedure for the determination of yttrium in yttrium earths after the separation of the cerite earths by precipitation with potassium sulphate.

Recently we have studied some displacement reactions which at first sight seem very promising for the differentiation of small groups of rare earths. Only two examples will be given here from the work in progress.

The sum of all rare earths present can be determined indirectly, *e.g.*, by back-titration with zinc solution at pH 5–5·5, with Xylenol Orange as indicator. When sodium phosphate at pH 5–6 is added in certain excess to the solution, some rare earths are quantitatively displaced by zinc according to the equation:

$$LnY^{-} + Zn^{2+} + PO_4^{3-} = LnPO_4 + ZnY^{2-} \qquad (3)$$

where Ln = La, Pr, Ce, Nd, and Y = anion of EDTA.

The heavier rare earths (Sm . . . Dy) are displaced very slowly and only partly, and the highest members (Ho . . . Lu) are not displaced at all (see Table II). With the

TABLE II.—DISPLACEMENT REACTIONS OF RE COMPLEXES BY ZINC TITRATION IN THE PRESENCE OF PHOSPHATES

RE	RE–EDTA + PO_4^{3-}	RE–EDTA + $P_2O_7^{4-}$	RE–HEDTA + PO_4^{3-}	RE–MEDTA + PO_4^{3-}	RE–HEDTA* + PO_4^{3-}	RE–TTHA + PO_4^{3-}	RE–DTPA + PO_4^{3-}
La	A	A	A	A	A	C	B
Ce	A	A	A	A	A	B	B
Pr	A	A	A	A	A	A	C
Nd	A	A	A	B	A	B	C
Sm	B	A	A	B	A	B	C
Eu	B	B	A	B	A	B	C
Gd	B	B	A	B	B	B	C
Tb	B	B	A	C	B	A	C
Y	B	B	A	C	B	—	C
Dy	B	B	B	C	B	B	C
Ho	C	B	B	C	B	A	C
Er	C	B	B	C	C	B	C
Tm	C	B	B	C	C	—	C
Yb	C	B	C	C	C	A	C

RE solution (2 ml, 0·05*M*) titrated with 0·05*M* complexing agent at pH 5–5·5 with Xylenol Orange as indicator, then 10 ml of 0·2*M* NaH_2PO_4 (or $Na_4P_2O_7$) added, and titrated with 0·05*M* zinc.

MEDTA = Methyl-EDTA = 1,2-diaminopropanetetraacetic acid.

A = quantitatively displaced; B = very slowly or not quantitatively displaced;

C = not displaced or not displaced by one drop during 5 min.

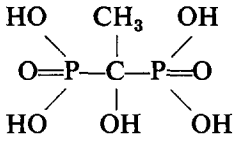
* Titrated with 0·05*M* cadmium.

aid of this displacement reaction some combinations of rare earths such as La–Tm, La–Er, Pr–Yb, Nd–Tm, Ce–Yb can be determined.[38]

Reaction (3) can be varied in many ways. For example, phosphate can be replaced by pyrophosphate or other complex-forming compounds, and EDTA by DCTA, MEDTA, HEDTA or TTHA (see Table II). However, unlike the EDTA complexes, the TTHA complexes of the light lanthanides are displaced either very slowly or

not at all by zinc in the presence of phosphate, while the higher rare earths are displaced more quickly. Unfortunately it is not possible to use this reaction because during the titration with zinc the displacement of the light lanthanides is "induced" by the faster reactions of the heavier rare earths. We have not been able so far to circumvent this difficulty.

More recently 1-hydroxy-ethylidene-1,1-diphosphonic acid (HEDPHA)—(I)—has been studied as a complex-forming reagent.



I

It forms a binuclear complex with thorium $(ThY)_2$-L, in the presence of EDTA or DCTA (where L is the anion of HEDPHA and Y the anion of EDTA or DCTA).[39]

Practical applications

Thorium and the sum of the rare earths present have been determined in monazite sands[34] and other materials.[40] Complexometric determination of rare earths in fission products[41] and in mixtures with alkaline earth oxides has been described.[42] Milner and Edwards[17] have determined neodymium and praseodymium in bismuth alloys, and Brück and Lauer[43] have determined lanthanum in aluminium alloys. A method for the determination of zirconium, thorium and lanthanum in non-silica glass has been published by Přibil and Veselý.[44]

Zussammenfassung—Es wird eine Übersicht über die visuelle komplexometrische Bestimmung von seltenen Erden, Scandium und Yttrium mit verschiedenen volumetrischen Reagentien gegeben. Wie in den früheren Teilen wird dem komplexometrischen Verhalten dieser Metalle und den Störproblemen bei ihrer Bestimmung besonderes Augenmerk geschenkt. Methoden zur Bestimmung von Thorium, Scandium und einigen seltenen Erden in Mischungen werden in Einzelheiten beschrieben. Neue Entwicklungen und zukünftige Möglichkeiten auf diesem Gebiet werden diskutiert.

Résumé—On présente une revue sur le dosage complexométrique visuel des terres rares, du scandium et de l'yttrium au moyen de divers réactifs volumétriques. Comme dans les parties précédentes, on prête attention au comportement complexométrique de ces métaux et aux problèmes des interférences dans leurs dosages. On décrit en détail des méthodes pour le dosage du thorium, du scandium et de quelques terres rares en mélanges. On discute de développements récents et de possibilités nouvelles dans ce domaine.

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SOLVENT EXTRACTION AND SEPARATION OF GALLIUM(III), INDIUM(III), AND THALLIUM(III) WITH TRIBUTYLPHOSPHATE

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Summary—A systematic study has been made of the solvent extraction behaviour of milligram amounts of gallium(III), indium(III), and thallium(III) with TBP from hydrochloric acid, and of thallium(III) from nitric acid, sulphuric acid and buffer solutions of different pH. The effect of the metal ion concentration, acid concentration, reagent concentration, salting-out agent, and diverse ions have been critically examined. A scheme for separation of gallium(III), indium(III), and thallium(III) from each other and for their determination is proposed.

A SYSTEMATIC study of the solvent extraction behaviour of gallium(III), indium(III), and thallium(III) with tributylphosphate (TBP) has been made and after a critical survey of the relevant factors, optimum conditions for the extraction have been determined.

Incomplete extraction of gallium(III) from hydrochloric acid with TBP has been reported.[1–3] The distribution ratios of indium(III) between TBP and hydrochloric acid have been measured.[4] The partial extraction of the iodo-complex of indium with TBP from nitric acid solution has been discussed.[5,6] Thallium(III) has been extracted with 50% TBP in n-decane and n-octane from aqueous sulphuric acid containing different concentrations of sodium chloride,[7] but the method is very time-consuming. Other reports include extraction of thallium with TBP from chloride, bromide and iodide solutions.[8,9] The distribution ratios of gallium(III), indium(III), thallium(I) and (III) *etc.*, extracted with TBP, as a function of hydrochloric acid concentration, have recently been reported.[10] The proposed methods for quantitative (>99%) extraction of gallium(III), indium(III) and thallium(III) with TBP from hydrochloric acid solution represent a definite improvement over the earlier methods and are more precise and rapid.

EXPERIMENTAL

Apparatus

The apparatus has been described previously.[11,12]

Reagents

Tributyl phosphate. The purification has been described previously.[11,12]

Gallium chloride solution, (5 mg of gallium/ml). Dissolve about 5 g of gallium chloride in 6*M* hydrochloric acid and make up to 500 ml with 6*M* hydrochloric acid. Standardize the solution by the oxine method.[13]

Indium chloride solution (2 mg of indium/ml). Dissolve about 2 g of indium chloride in 0·5*M*

hydrochloric acid and make up to 500 ml with 0·5*M* hydrochloric acid. Standardize the solution by the oxine method.[18]

Thallium(I) nitrate solution (10 *mg of thallium/ml*). Dissolve about 6·5 g of thallium nitrate in 1*M* nitric acid and make up to 500 ml with 1*M* nitric acid. Standardize the solution gravimetrically by the chromate method.[14]

Buffer solutions. Prepare by standard procedures: pH 2 (chloroacetate); pH 3·2 (acetate–hydrochloric acid); pH 4–6 (acetate–acetic acid).

The chemicals used were either chemically pure or reagent grade materials unless otherwise mentioned.

General procedure

The procedures were similar to those reported previously.[11,13] The following table summarizes the extraction conditions and analytical procedures.

TABLE I.—SUMMARY OF EXTRACTION CONDITIONS AND PROCEDURES

	Ga	In	Tl
Aqueous phase	Ga, 20 mg HCl, 0·35–6*M* (final) Total volume, 20 ml	In, 10 mg HCl, 0·1–9·1*M* (final) Total volume, 20 ml	Tl(I), 20 mg (oxidize with Br_2-water, warm, and cool) HCl, 0·1–6*M* (final) or HNO_3, 0·5–6*M* (final) or H_2SO_4, 0·25–5*M* (final) or buffer solution, pH 2–6. Total volume, 20 ml
Organic phase	TBP, 100%, 10 ml (acid-saturated)	TBP, 100%, 10 ml (acid-saturated)	TBP, 100%, 10 ml (acid-saturated)
Shaking period	2 min	2 min	10 min
Scrubbing (during salting-out effect and diverse ion studies)	4*M* HCl, 2 × 20 ml	6*M* HCl, 2 × 20 ml	2*M* HCl, 2 × 20 ml
Stripping agents	HCl, 0·02*M* (3 × 20 ml)	H_2O (2 × 20 ml) or tartaric acid (6·3%)–4*M* NH_3 (20 ml) followed by H_2O (20 ml).	20-vol H_2O_2 (12·5%)–3*M* NH_3 (20 ml) followed by H_2O_2 (5%)–3*M* NH_3 (20 ml)
Analysis	Complexometric titration[15]	Complexometric titration[15]	Complexometric titration[15] (decompose H_2O_2, then oxidize with Br_2-water, warm, and cool)

RESULTS AND DISCUSSION

Effect of acidity

The TBP extraction of gallium(III), indium(III), and thallium(III), as a function of hydrochloric acid concentration, was investigated. The extraction of thallium(III) was also investigated at varying concentration of nitric acid and sulphuric acid and over the pH range 2 to 6. The distribution ratio, *D*, was calculated as the ratio of the total metal ion concentrations in the organic and aqueous phases, determined by complexometric titration.[15] The results were also verified under optimum conditions of extraction by using larger amounts of the metals (20–25 mg) and checking the values by conventional gravimetric methods.

Table II and Fig. 1 show that the extraction of all three metals with 100% TBP increases with increasing acid concentration, and becomes quantitative for gallium from 2·0–6·0*M* hydrochloric acid, for indium(III) from 6·1–8·1*M* hydrochloric acid and for thallium(III) from 1·0–6·0*M* hydrochloric acid. For acid concentrations

TABLE II.—DISTRIBUTION RATIOS AS A FUNCTION OF HYDROCHLORIC ACID CONCENTRATION

HCl, *M* (initial)	*D*		
	Ga*	In*	Tl*
0·10	—	no extraction	112
0·35	2·1	—	—
0·50	—	—	343
0·60	3·9	0·7	—
1·15	14·2	3·3	Complete extn.
1·50	—	—	Complete extn.
2·10	Complete extn.	23·0	Complete extn.
4·10	Complete extn.	48·1	Complete extn.
6·10	Complete extn.	240	Complete extn.
8·10	—	112	—
9·10	—	48·1	—

* Ga = 20·10 mg; In = 10·89 mg; Tl = 20·70 mg; TBP 100%.

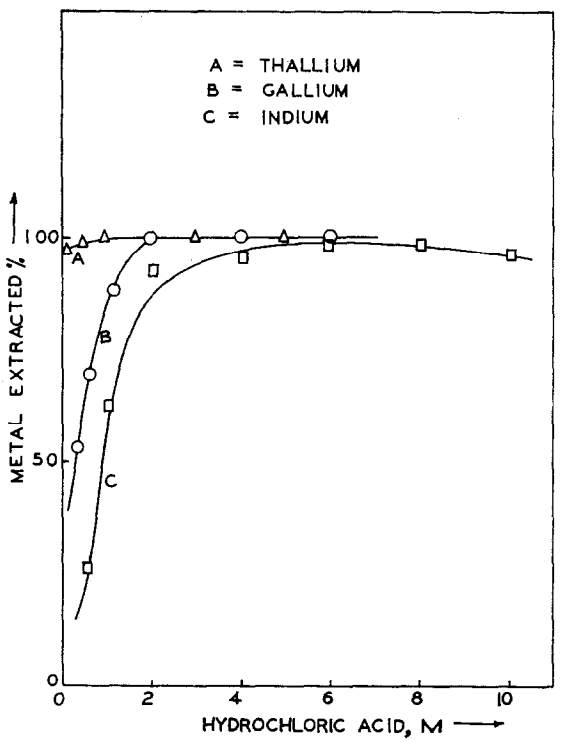

FIG. 1.—Extraction with TBP as a function of hydrochloric acid concentration.

$>8{\cdot}1M$ the extraction of indium(III) decreases. The concentrations given are the initial concentrations; the equilibrium concentrations are $<1\%$ lower.

Table III shows that the extraction of thallium(III) increases with increasing nitric acid concentration, reaches a maximum of 84·5% at $2{\cdot}0M$ nitric acid (initial) and then decreases with further increase in acid concentration. The extraction of thallium(III) increases with increasing sulphuric acid concentration and decreasing

TABLE III.—DISTRIBUTION RATIO OF THALLIUM AS A FUNCTION OF pH OR NITRIC AND SULPHURIC ACID CONCENTRATION

pH (initial)	Distribution ratio, *D*	HNO_3, *M* (initial)	Distribution ratio, *D*	H_2SO_4, *M* (initial)	Distribution ratio, *D*
2·20	29·4	0·5	7·7	0·25	1·7
3·20	11·7	1·0	9·2	1·0	2·3
6·05	1·3	2·0	10·9	2·0	3·1
		4·0	7·1	3·0	3·6
		6·0	5·0	4·0	5·0

Tl = 20·70 mg; TBP = 100%.

pH of the solution. As a safety precaution, further investigation with more concentrated sulphuric acid was avoided.

To study the effect of the metal ion concentration on extraction the amount of the metal ion was varied from 5 to 30 mg under the optimum conditions and it was found that the recommended method of extraction holds good. Varying the metal ion concentration under conditions of incomplete extraction gave almost constant values of *D* indicating the absence of polymerization in the organic phase for up to 30 mg of the metal ion.

Effect of TBP concentration

The effect of the reagent concentration was investigated by varying the concentration of TBP from 3% (0·109*M*) to 100% (3·66*M*). Benzene was used as the diluent. Table IV shows that the extraction of gallium(III), indium(III) and thallium(III) increases with increasing TBP concentration in the organic phase. The extraction of gallium(III) becomes quantitative with 20%, 25% and 100% TBP from

TABLE IV.—DISTRIBUTION RATIO OF GALLIUM, INDIUM AND THALLIUM AS A FUNCTION OF TBP CONCENTRATION

TBP concentration* %	Ga†	In‡	Tl**	Tl††
3	—	—	0·24	—
5	0·16	—	1·03	5·0
7	—	—	2·31	6·63
8	0·76	—	3·89	—
10	2·22	0·13	7·34	9·57
15	9·14	—	complete extn.	11·7
20	41·0‡‡	0·67	complete extn.	—
25	complete extn.	—	complete extn.	—
30	complete extn.	3·57	complete extn.	—
40	complete extn.	14·8	complete extn.	—
50	complete extn.	48·1	complete extn.	—
100	complete extn.	complete extn.	complete extn.	—

* Benzene diluent.
† Aqueous phase, 4*M* HCl; Ga, 20·10 mg.
‡ Aqueous phase, 6*M* HCl; In, 10·89 mg.
‡‡ Complete extraction from 6*M* HCl.
** Aqueous phase, 2*M* HCl; Tl, 20·70 mg.
†† Aqueous phase, acetate buffer (pH 6·05); Tl, 20·70 mg.

6*M*, 4*M* and 2*M* hydrochloric acid respectively. The extraction of gallium(III) with 20% TBP from 2*M* hydrochloric acid is poor. This indicates that though the dilution of TBP lowers the extraction of gallium(III), an increase in acid concentration increases it again. The extraction of indium(III) becomes quantitative with 100% TBP at 6*M* hydrochloric acid and dilution of the TBP lowers the extraction. The extraction of thallium(III) becomes quantitative with 15% TBP (0·549*M*) from 2*M* hydrochloric acid.

The general extraction reaction for these tervalent cations can be expressed according to Diamond and Tuck[16] as $M^{3+} + 3\ Cl^- + 3\ TBP_{(o)} \rightleftharpoons [MCl_3.(TBP)_3]_{(o)}$ and if the concentration of hydrochloric acid is high enough, the species extracted is probably $HMCl_4.3$ TBP. In the case of gallium and indium, because of the very small values of D at low TBP concentrations (<10%), attempts at log D–log C_{TBP} plots were not successful. Only with thallium were measurable values of D obtained at low TBP concentrations, and the extracted species (from 2*M* hydrochloric acid) is presumably $TlCl_3.3TBP$. The recommended optimum TBP concentrations for extraction are: gallium 20–100%; indium 100%; thallium 20–100%.

Salting-out effect

Ammonium chloride or magnesium chloride in the aqueous phase exerts a salting-out effect leading to enhanced extraction of gallium, indium or thallium.

TABLE V.—EFFECT OF AMMONIUM CHLORIDE AS SALTING-OUT AGENT

Metal ion*	Acidity	Distribution ratio, D		
		1*M* NH_4Cl†	2*M* NH_4Cl	4*M* NH_4Cl
Ga	1·2*M* HCl	110·1	Complete extraction	Complete extraction
In	1·1*M* HCl	8·4	18·0	38·3
Tl	pH 6·0 (acetate buffer)	37·8	108	Complete extraction

* Gallium = 20·10 mg; Indium = 10·89 mg; Thallium = 20·70 mg: TBP = 100%.
† The values of D in absence of NH_4Cl are 14·2 (Ga), 3·3 (In) and 1·3 (Tl).

Diverse ions

The ions examined were Ni, Mn(II), Cu(II), Co(II), Pb, Hg(II), Sn(II), Sn(IV), Pd(II), Bi, Al, Sb(III), V(V), Ag, Fe(III), U(VI), W(VI), fluoride, borate, citrate, tartrate, phosphate, thiocyanate and EDTA. Mutual interference of gallium, indium and thallium is eliminated by the separation procedure. The tolerance limit was set at 10 mg or less for ions which interfere.

The extractions were carried out according to the recommended procedure to examine the interference of ions usually associated with gallium, indium and thallium. In each experiment the organic phase, after extraction, was scrubbed with two 20-ml portions of the appropriate acid (gallium, 4*M* hydrochloric acid; indium, 6*M* hydrochloric acid; thallium, 2*M* hydrochloric acid) to remove the slightly co-extracted and entrained ions.

Gallium(III). Except for iron(III) and uranium(VI) none of the ions tested is extracted under the same conditions as gallium(III). The interference of iron(III) is eliminated by reducing to iron(II) with ascorbic acid. The trace amount of uranium(VI)

extracted is removed by scrubbing with four 20-ml portions of 4*M* hydrochloric acid. Tungsten(VI) (20 mg) remains in the aqueous phase in the presence of tartaric acid, and silver (5 mg) is not extracted from 6*M* hydrochloric acid containing ammonium persulphate. The interference of fluoride ion can be eliminated by extraction from a more acidic medium (6*M* hydrochloric acid).

Indium(III). A large number of metal ions are to some extent extracted under the the same conditions as indium(III), but many can be removed by scrubbing with two 20-ml portions of 6*M* hydrochloric acid. Among those which persist after this treatment are: copper(II), cobalt(II), tin(II) (2 mg), tin(IV), silver, antimony(III) and bismuth(III) (5 mg). They can be removed by scrubbing with four 20-ml portions of 6*M* hydrochloric acid. Palladium(II), iron(III), vanadium(V), uranium(VI) and tungsten(VI) are also extracted, but in the presence of tartaric acid vanadium(V) (10 mg) is not extracted and 2 mg of iron(III) can be tolerated if ascorbic acid is added.

Thallium(III). Only trace amounts of iron(III) and uranium(VI) are extracted under the same conditions as thallium. The interference of iron(III) is eliminated by masking with fluoride ion and that of uranium(VI) is removed by scrubbing with three 20-ml portions of 2*M* hydrochloric acid. The interference of tin(II), which tends to reduce thallium(III) to thallium(I), is eliminated by oxidizing with bromine water. Tungsten(VI) remains in the aqueous phase in the presence of tartaric acid, and silver is not extracted from 6*M* hydrochloric acid containing ammonium persulphate.

Recommended procedures

These results led to the following recommended procedures. All determinations are completed as outlined in Table I. Interfering ions should be removed or dealt with as described.

Extraction scheme for separation and estimation of gallium(III), indium(III) and thallium(III). Take in a 100-ml separating funnel, 10 ml of a solution containing about 10 mg of each of the metals and add 10 ml of 4*M* hydrochloric acid and 10 ml of 20% TBP in benzene. Shake the mixture for 10 min. Only thallium(III) is extracted. Separate the phases and keep the aqueous phase. Scrub the organic phase with 20 ml of 2*M* hydrochloric acid and add the washings to the aqueous phase. Strip thallium(III) from the organic phase and determine it as described. To the combined aqueous phases add 0·3 ml of 10% sodium chloride solution and evaporate almost to dryness. Dissolve the residue in 20 ml of 6*M* hydrochloric acid and extract for 2 min with 10 ml of 20% TBP in benzene previously saturated with 6*M* hydrochloric acid. Scrub the organic phase with three 20-ml portions of 6*M* hydrochloric acid to remove any indium. Separate the phases and strip gallium(III) from the organic phase and determine it as before.[15] Determine indium(III) in the combined aqueous phases.[15]

Typical results are shown in Table VI.

TABLE VI.—SEPARATION AND DETERMINATION OF GALLIUM, INDIUM AND THALLIUM

Taken, mg					
Ga		In		Tl	
Taken, *mg*	Found, *mg*	Taken, *mg*	Found, *mg*	Taken, *mg*	Found, *mg*
10·05	10·15	10·89	10·90	10·35	10·33
10·05	10·02	10·89	10·85	10·35	10·36
10·05	10·10	10·89	10·92	10·35	10·35

Gallium. Place an aliquot of chloride solution, containing up to 30 mg of gallium, in a 100-ml separating funnel, add 10 ml of 8*M* hydrochloric acid, and dilute to 20 ml. Shake for 2 min with 10 ml of 25% TBP in benzene previously saturated with 4*M* hydrochloric acid. Allow the phases to separate. Scrub the organic phase with 4*M* hydrochloric acid (2 × 10 ml), strip with 0·02*M* hydrochloric acid (3 × 20 ml) and determine gallium as above.

Indium. Place an aliquot of chloride solution, containing up to 30 mg of indium, in a 100-ml separating funnel, add 10 ml of concentrated hydrochloric acid and dilute to 20 ml. Extract for 2 min

with 10 ml of 100% TBP previously saturated with 6*M* hydrochloric acid. Allow the phases to separate and proceed as described in Table I.

Thallium. Place an aliquot of nitrate solution, containing up to 30 mg of thallium, in a 50-ml beaker, add a few drops of bromine water, warm to remove the excess of bromine, cool, and transfer into a 100-ml separating funnel quantitatively with 5 ml of water. Add 10 ml of 4*M* hydrochloric acid and dilute to 20 ml. Mix well and shake the aqueous phase with 10 ml of 20% TBP in benzene for 10 min. Allow the phases to separate and proceed as described before.

Zusammenfassung—Das Extraktionsverhalten von Milligrammengen Gallium(III), Indium(III) und Thallium(III) mit TBP aus Salzsäure sowie von Thallium(III) aus Salpetersäure, Schwefelsäure und Pufferlösungen verschiedenem pH wurde systematisch untersucht. Der Einfluß der Konzentrationen von Metallion, Säure, Reagens, Aussalzmittel und verschiedenen Ionen wurde kritisch geprüft. Ein Schema zur Trennung von Gallium(III), Indium(III) und Thallium(III) voneinander und für ihre Bestimmung wird vorgeschlagen.

Résumé—On a étudié systématiquement le comportement à l'extraction par le TBP de quantités de l'ordre du milligramme de gallium(III), indium(III) et thallium(III) à partir d'acide chlorhydrique et de thallium (III) à partir d'acide nitrique, d'acide sulfurique et de solutions tampons de différents pH. On a étudié de façon critique les influences des concentrations en ion métallique, acide et réactif, ainsi que celles de l'agent de relargage et de divers ions. On propose un schéma pour la séparation du gallium (III), de l'indium(III) et du thallium(III) l'un de l'autre et pour leur dosage.

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DETERMINATION OF PLUTONIUM OXIDATION STATES IN DILUTE NITRIC ACID BY COMPLEMENTARY TRISTIMULUS COLORIMETRY

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Summary—The preparation of reference standards for use in complementary tristimulus colorimetry for plutonium is described. Plutonium(III) and (VI) are prepared by hydrazine reduction and silver(II) oxidation, respectively, of plutonium(IV). Plutonium(V) is prepared by reduction of plutonium(VI) with ascorbic or sulphurous acid. A method for computerizing tristimulus colorimetry is presented, and the technique is extended to three dimensions ("quadristimulus colorimetry").

MUCH attention was given to the determination of the oxidation states of plutonium in aqueous solutions when macro amounts of this element became available several years ago.[1,2] From time to time since then various methods have been suggested for determining the various species of plutonium in solution.[3,4] The method described in this paper is based on the work of Reilley *et al.*,[5,6] and has been extended to include four species. All the work described in this paper was performed with solutions of plutonium-238, a Beckman DK-2A spectrophotometer being used. Limitations on our facilities precluded use of all but the 238 isotope, and the techniques here described were later used to study plutonium-238 in dilute nitric acid.

DISCUSSION

The analysis of plutonium-238 in dilute nitric acid solution (0·2–1·0*M*) has been approached spectrophotometrically by the method of abbreviated complementary tristimulus colorimetry. The advantages of this technique have been described by Reilley.[6] While the multi-wavelength approach to the analysis of three-component mixtures would probably have been more accurate, the abbreviated method has been found to be rapid, convenient, and sufficiently accurate for most purposes. A spectrophotometric method is appropriate for plutonium solutions because the instrumentation is generally available and because the three principal oxidation states of plutonium [*i.e.*, plutonium(III), (IV) and (VI)] are all coloured species. For these studies the visible region of the spectrum was selected, and the range 860–420 mμ has been routinely used. This spectral region is not necessarily the best region for monitoring plutonium solutions, but was selected because of the limitations of our instrumentation.

In order to use the complementary colorimetry technique for the analysis of mixtures of Pu(III), Pu(IV), and Pu(VI), it was necessary to prepare standard solutions of these species. The preparation of plutonium in various oxidation states has been

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examined in detail and the methods herein described, with some modification, have been adapted from standard methods.[1,2,7] Complementary colour points and C° values of Pu(III), Pu(IV), and Pu(VI) vary somewhat with the particular spectrophotometer used. Hence, values of the colour point (x, y) and C° are given to only two significant figures. Complementary colour points for Pu(III), Pu(IV), and Pu(VI) are essentially unchanged over the concentration range 0·2–1·0M nitric acid. The colour point of Pu(V) was not examined at this acidity, because of the instability of Pu(V) at this acid concentration. The terms are defined as:

$$x = \frac{A_{475}}{A_{475} + A_{525} + A_{560}}$$

$$y = \frac{A_{525}}{A_{475} + A_{525} + A_{560}}$$

C° = unit of concentration for which the colour concentration (J) is unity

where A is the absorbance at the wavelength (in mμ) indicated by subscript.

The visible spectra of the plutonium(III), (IV) and (VI) species have already been published.[1,2,9] Examination of these spectra reveals, for the tervalent and quadrivalent states, a variety of wavelengths suitable for spectrophotometric use. Unfortunately, the visible spectrum of Pu(VI) is neither as intense nor as rich as the visible spectra of the Pu(III) and Pu(IV). Spectrophotometry of PuO_2^{2+}, for these reasons, is accompanied by more difficulties than is that of the tervalent and quadrivalent species. In these studies, many of the errors encountered can be traced in part to the relative poverty of the visible spectrum of PuO_2^{2+} (*i.e.*, the absorption of light is rather weak and C° is thus rather large). Small errors in either q_{VI}° (where q_{VI}° is the "colour fraction" of Pu present as PuO_2^{2+}) or J thus result in significant errors in the calculated amount of Pu(VI). This is particularly true in solutions containing only a small amount of Pu(VI). In such cases it may be advantageous to determine the concentration of Pu(VI) by difference.

In this study, the wavelengths selected for analysis were 475, 525 and 560 mμ. Doubtless other wavelengths could also be used. The first wavelength, 475 mμ, corresponds to the maximum of a sharp peak in the spectrum of Pu(IV). Although this peak is quite sharp, and requires delicate setting of the spectrophotometer, it has been found to be useful. This wavelength corresponds to the side of an absorption band of Pu(VI). The wavelength 525 mμ was selected because it is the only other useful absorption band in the visible spectrum of Pu(VI). The wavelength 560 mμ corresponds to the top of a relatively broad absorption band of Pu(III).

A check on the accuracy of the quantities of Pu(III), Pu(IV) and Pu(VI) determined by this complementary colorimetry technique is the agreement between the total quantity of plutonium present, which with plutonium-238 is easily ascertained by alpha-counting, and the sum of the values of the three species obtained by spectrophotometry. In this respect we find our mass agreement similar to that given by Reilley and Smith.[6]

EXPERIMENTAL

Plutonium(III)

Solutions of plutonium(IV) in nitric acid were evaporated to incipient dryness (*i.e.*, to the formation of crystals), cooled and diluted with 0·2–0·5M nitric acid. As the concentration of the nitric acid

is increased, it is increasingly difficult to maintain solutions of Pu(III) free from other oxidation states. To this solution was then added a small amount of hydrazine neutralized with nitric acid, and the solution was gently boiled to reduce the plutonium to the tervalent state. Immediate measurement of the spectrum of a solution so prepared was desirable since aged solutions of tervalent plutonium-238 containing both hydrazine and nitric acid gradually become red. However, it was necessary to cool the solution before measurement because the spectrum of Pu(III) was found to be somewhat temperature-dependent.[8] The complementary colour point and unit of colour concentration of Pu(III) are (0·10, 0·07) and $C^\circ = 15{\cdot}5$ mg/ml.

Plutonium(IV)

Reference spectra of Pu(IV) were measured for solutions obtained by evaporating solutions of plutonium(IV) nitrate in nitric acid to the formation of crystals, cooling, and diluting with dilute nitric acid. During this evaporation of the solution, there is the danger that the evaporation will occur at a temperature sufficient to cause accidental denitration of the crystals resulting in oxidation to the sexivalent state:

$$Pu(NO_3)_4 \rightleftarrows PuO_2(NO_3)_2 + 2NO_2.$$

Conversely, heating at lower temperatures causes the evaporation time to become unduly lengthy. If the crystals are successfully obtained free from plutonium(VI), there is the danger of oxidation by dilute nitric acid upon dilution if the crystals have not been sufficiently cooled. More troublesome difficulties are encountered in attempting to ascertain what concentration of nitric acid should be used for dilution. If the acid is too dilute, hydrolysis of Pu(IV) is a problem, as may be the disproportionation of the quadrivalent state which begins immediately in dilute acid. Hydrolysis and precipitation do not occur if the cooled crystals are carefully dissolved in 0·5*M* nitric acid. The complexation of Pu(IV) by nitrate is such that in nitric acid that is between 0·2*M* and 1·0*M*, the fraction of $Pu(NO_3)^{3+}$ changes significantly, presumably resulting in accompanying spectral changes.[8] In this study, Pu(IV) in 0·5*M* nitric acid has generally proved satisfactory as a standard for the acidity range 0·2–1·0*M*. The problem of preparing Pu(IV) is particularly bothersome since it would be desirable to have one reference spectrum serve for a variety of nitric acid solutions. For plutonium(IV) the colour point and unit of colour concentration are approximately (0·76, 0·12) and 8·6 mg/ml.

Plutonium(VI)

Reference solutions of PuO_2^{2+} were prepared by evaporating plutonium(IV) nitrate in nitric acid to crystals and diluting with a small amount of 1*M* nitric acid. Small portions of silver(II) oxide were then added to oxidize the plutonium to the sexivalent state. When enough silver oxide had been added to impart a dark cast to the solution, oxidation was considered complete and the solution was allowed to stand in air for several hours to ensure reduction of the excess of silver(II). The solution was then diluted with 0·3*M* nitric acid. Small amounts of unreduced silver or other coloured impurities render a spectrum of PuO_2^{2+} untenable as a standard. The colour point and unit of colour concentration of Pu(VI) are approximately (0·43, 0·48) and 28 mg/ml.

Plutonium(V)

Some literature on plutonium notwithstanding,[11] the spectrum of Pu(V) proved one of the easiest reference spectra to obtain. Plutonium(V) is easily prepared from solutions of plutonyl nitrate which are silver-free. A small amount of such silver-free plutonyl nitrate was neutralized with ammonia solution (1 + 1) until one tiny drop of base turned the solution deep yellow-brown. If allowed to stand for several minutes, such neutralized solutions are likely to hydrolyse. It is necessary to neutralize the solution before reduction, however, because of the tendency of PuO_2^+ to disproportionate below pH 2 and because the reduction of PuO_2^{2+} in highly acid solution would result in reduction to the quadrivalent state. Ammonia was selected as a neutralizing agent because it forms its own buffer as the neutralization nears completion and prevents the pH from rising much above 8, thus minimizing the risk of hydrolysis. Immediately after neutralization, a 0·1*M* solution of ascorbic acid was added dropwise. This reagent, apparently not used before in the preparation of Pu(V), is both a reducing agent and an acid. Its acidic properties render it a buffer in the region of pH 4, which is ideal for the preparation of PuO_2^+. Its reducing properties also allow formation of the pink plutonium(V) species from the orange-pink plutonium(VI) species.

Numerous reagents have been used to prepare PuO_2^+, among them sulphite and iodide.[7,11] Iodine must be extracted from the solution if iodide is used as a reducing agent, and there is some evidence that sulphite solutions containing sulphate may complex Pu(V).[11] Ascorbic acid is not a good complexing agent, however, and it need not be removed from the solution before the spectrophotometric analysis. Plutonium(V) was also prepared by use of sulphur dioxide, and the spectrum

of the plutonium(V) so prepared compared favourably with that obtained when ascorbic acid was used. The colour point of Pu(V) is not used in complementary tristimulus colorimetry in these studies.

CALCULATIONS

The graphical method of tristimulus calculations of data points, although lengthy, is adequate for plutonium solutions. Methods of calculation are discussed by Flaschka.[12,13] For expediency, the tristimulus calculations were translated into Fortran II for processing on an IBM 1620 computer. The q° values were calculated by the method of the ratio of perpendiculars, as illustrated in Fig. 1. This diagram illustrates a sample calculation of q_1° based on the ratios of the perpendicular distances of the data point from the line (2–3) and of the point (1) from line (2–3) ($q_1^\circ = h_2/h_1$). The reference points were stored in the computer memory and converted to the proper co-ordinates before analysis of the data points, which were calculated from solution absorbance values used as input data.

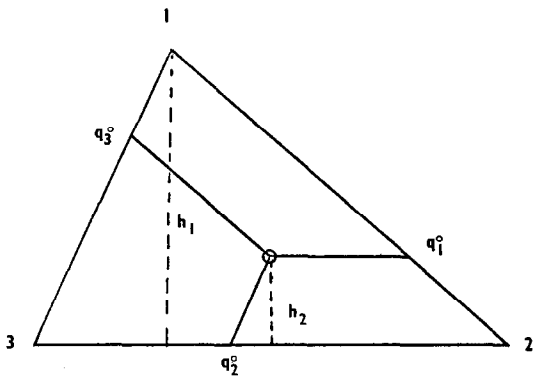

FIG. 1.—Method of calculating q_1.

In order to examine spectra for the presence of a fourth species, the method of complementary tristimulus colorimetry was expanded to three dimensions. The resulting geometric figure in which data points are located is a pyramid, the four vertices of this pyramid having been determined by the absorbance values of Pu(III), Pu(IV), Pu(V) and Pu(VI) at 475, 525, 560 and 600 mμ. In this method the ratio calculations were also performed by computer. Any two reference points serve to define one edge of the pyramid; three reference points define two vectors, the cross-product of which is a vector perpendicular to the plane defined by the three reference points. This plane is one side of the pyramid. The perpendicular distance of a data point from one of the faces of the pyramid is found by projecting the vector defined by one of the original reference points and the data point, onto the vector defined by the cross-product of the vectors derived from three reference points. Thus,

$$V(\cos\theta) = d = \frac{(A \times B) \cdot (V)}{A \times B}$$

where: A, B = vectors defined by three reference points
V = vector defined by the data point and one reference point
d = perpendicular distance of the data point from the plane defined by three reference points.

By use of the absorbance values at 475, 525 and 560 mμ as the numerator in determining the x, y, and z co-ordinates respectively, the following points and reference concentration values were obtained:

Pu(III): (0·04, 0·02, 0·48), $C^\circ = 12$ mg/ml
Pu(IV): (0·72, 0·11, 0·12), $C^\circ = 11$ mg/ml
Pu(V): (0·19, 0·24, 0·38)
Pu(VI): (0·40, 0·46, 0·10), $C^\circ = 36$ mg/ml

Acknowledgement—The author wishes to thank F. C. Fushimi and M. S. Mowchan for their thoughtful suggestions and help during the course of this work.

Zusammenfassung—Die Herstellung von Vergleichsstandards zum Gebrauch bei der komplementären Tristimulus-Kolorimetrie von Plutonium wird beschrieben. Plutonium(III) und -(VI) werden durch Reduktion von Plutonium(IV) mit Hydrazin bzw. Oxydation mit Silber(II) hergestellt, Plutonium(V) durch Reduktion von Plutonium(VI) mit Ascorbin- oder schwefliger Säure. Es wird eine Methode vorgestellt, die Ergebnisse der Tristimulus-Kolorimetrie im Computer zu verarbeiten, und das Verfahren wird auf drei Dimensionen ausgedehnt ("Quadristimulus-Kolorimetrie").

Résumé—On décrit la préparation d'étalons de référence pour l'emploi dans la colorimétrie en tristimulus complémentaire du plutonium. On prépare les plutonium(III) et (VI) par réduction à l'hydrazine et oxydation à l'argent(II), respectivement, du plutonium(IV). On prépare le plutonium(V) par réduction du plutonium(VI) aux acides ascorbique ou sulfureux. On présente une méthode pour la mise en calcul de la colorimétrie en tristimulus, et étend la technique à trois dimensions ("colorimétrie en quadristimulus").

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POLAROGRAPHIC DETERMINATION OF METHYL METHACRYLATE

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Summary—The permanganate oxidation of methyl methacrylate in weakly acidic solution yields methyl pyruvate. Hydroxylamine hydrochloride is used for destroying the excess of permanganate. At the same time it is consumed for oximation of the pyruvate, and the resulting oxime is determined polarographically. The reaction scheme of permanganate oxidation of methyl methacrylate is suggested and optimum working conditions are found both for permanganate oxidation and for polarographic determination. The method is used for the determination of vapours of methyl methacrylate in the air, for industrial hygiene purposes.

ANALYTICAL methods for the determination of methyl methacrylate are based on spectrophotometry in the infrared[1,2] or ultraviolet region,[1,3] gas chromatography,[4,5] polarography[6–8] and on the addition of halogens,[1,9] mercaptans[10] or mercury compounds[11] to the double bond. Indirect photometric methods are based on the photometry of the iron(III) salt of hydroxamic acid.[12] Oxidation methods are based either on the complete oxidation of the ester to carbon dioxide and water[13] with titrimetric determination of the remaining oxidation reagent, or on the fission of the double bond, the end carbon atom of the double bond yielding formaldehyde; either the remaining oxidation reagent[14] or the liberated formaldehyde[15] is then estimated.

This paper deals with the mechanism and analytical application of the permanganate oxidation of methyl methacrylate in a slightly acidic solution.

EXPERIMENTAL

Apparatus

For the polarographic determination Heyrovský's recording polarograph type V301 and reflecting galvanometer type Z9 of sensitivity $1{\cdot}4 \times 10^{-9}$ A were used. The samples were analysed under nitrogen in short cells with a needle-type SCE and Smoleř's dropping mercury electrode. The flow-rate of mercury was 0·55 mg/sec. The drop-time, measured in a $0{\cdot}64 \times 10^{-3}M$ solution of methyl pyruvate oxime, at 1·2 V and at 40·3 cm mercury height was 3·00 sec.

For the estimation of pH, a Beckmann compensation pH-meter was used.

Reagents

For the preparation of hydrochloric acid-potassium chloride buffers, 50 ml of $0{\cdot}2M$ potassium chloride were mixed with different amounts of $0{\cdot}2M$ hydrochloric acid and made up to 200 ml with distilled water.

Walpole's $0{\cdot}2M$ acetate buffer solution: different amounts of $0{\cdot}2M$ acetic acid were made up to 100 ml with $0{\cdot}2M$ sodium acetate.

The methyl pyruvate[16] and methyl acetate[17] were prepared by standard methods. The esters and pyruvic acid were freshly distilled before use.

Development of method

In most experiments, measured amounts of standardized permanganate solution and acid or buffer solution were made up with water to 4·5 ml. To this oxidation mixture 0·5 ml of standard ester

solution was added. After a definite time, the oxidation was stopped by addition of 1 ml of acid hydroxylamine hydrochloride solution and the oxime obtained was determined polarographically. The maximum on the polarographic waves was suppressed by addition of 0·05 ml of 0·5% tylose solution.

For determination of the amount of permanganate necessary for the oxidation, a titrimetric determination of unreacted permanganate[18,19] was carried out in addition to the polarographic determination of the methyl pyruvate oxime. To a series of solutions of different permanganate content (total volume 12·5 ml), 2·5 ml of 0·05*N* sulphuric acid and 10 ml of aqueous methyl methacrylate solution (25 μmole) were added. Immediately after mixing, 5 ml of each solution were measured into a separate flask. After 24 hr at 20° these 5-ml portions were analysed polarographically and to the remaining 20 ml of solution 10 ml of 0·5*M* manganese sulphate, 4 ml of 4*N* sulphuric acid, 30 ml of a saturated solution of sodium pyrophosphate, 30 ml of distilled water and 3 drops of 1% diphenylamine (in sulphuric acid) were added and they were titrated with 0·1*N* hydroquinone, standardized with dichromate. The result was calculated for 5 μmole of ester.

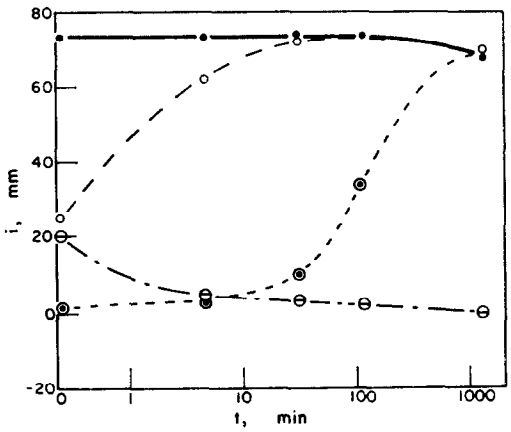


FIG. 1.—Rates of oxidation of equal amounts (0·82 mmole) of various substances. ○—methyl methacrylate (0 mm); ●—methyl pyruvate (70·7 mm); ⊙—methyl lactate (0 mm); ⊖—pyruvic acid (74·0 mm). The heights of the polarographic waves (galvanometer sensitivity 1/20) correspond to the amounts of oxime produced on oxidation at 22°C with 0·02*N* permanganate in 0·005*N* sulphuric acid. The heights of the polarographic waves of the starting material are given in brackets.

RESULTS AND DISCUSSION

The mechanism of methyl methacrylate oxidation

To explain the oxidation mechanism of methyl methacrylate in slightly acid solution (0·005*N* sulphuric acid), the end product of oxidation was isolated and identified, and the kinetics of oxidation of methyl methacrylate at low temperature, and of the oxidation of pyruvic acid, methyl pyruvate and methyl lactate were followed, for these compounds can be considered as possible products of the oxidation of methyl methacrylate.

Hydroxylamine hydrochloride in a solution of 1*M* sodium hydroxide[20] was used for the preparative oximation of methyl pyruvate. The product was extracted with ether, the ether was evaporated and the product was refined by sublimation twice at normal pressure, and dried over silica gel. The half-wave potential and the characteristic polarographic wave of this product are in accord with the properties of the oxime of the product resulting from the oxidation of methyl methacrylate. The melting point of the product is 73·3°. (Literature values: m.p. = 68–69° after crystallization from ether[21] or m.p. 71° after crystallization from benzene.[22]) Elemental

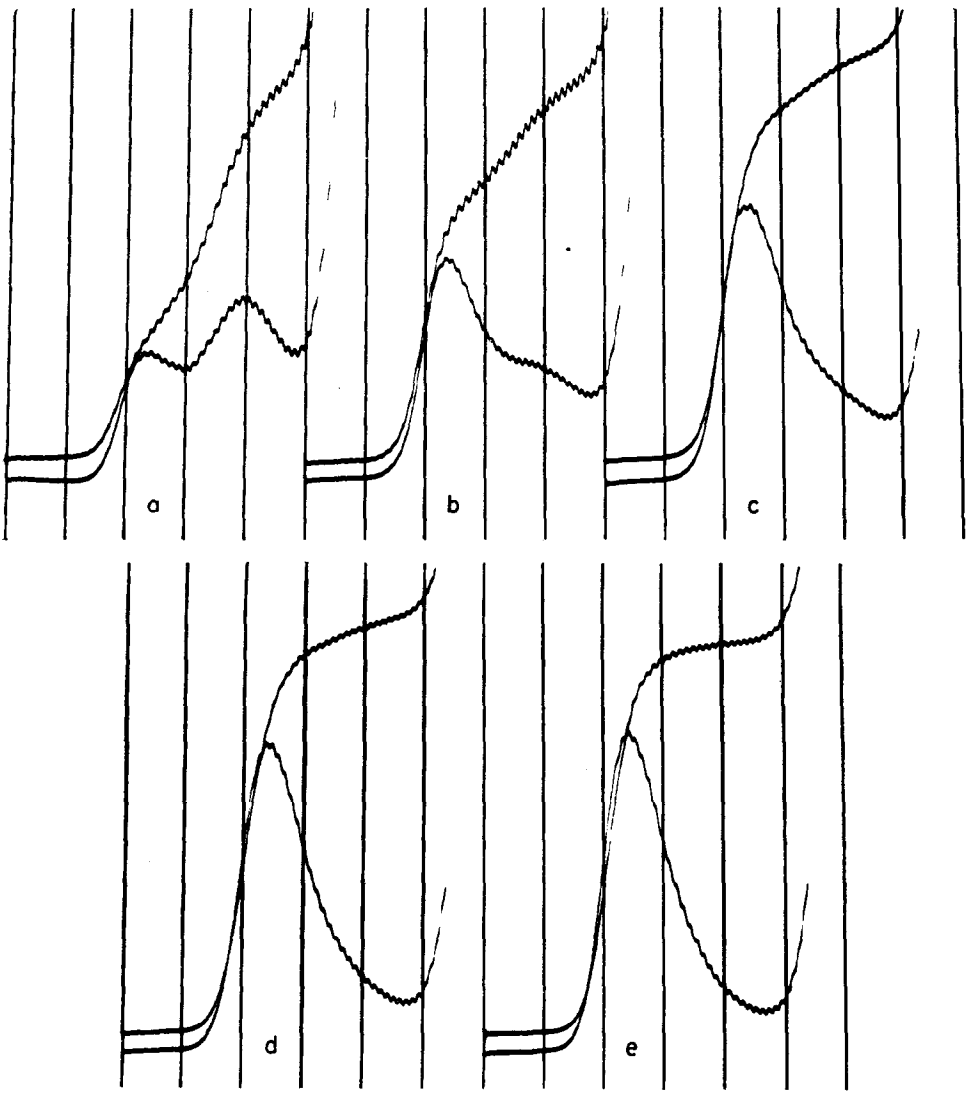


FIG. 2.—Rate of oxidation of methyl methacrylate (1·21 mmole). Direct and derivative polarographic curves for the oxime are shown. Galvanometer sensitivity 1/30; oxidation as for Fig. 1. *a*—5 sec oxidation at 5°C; *b, c, d, e*—5, 10, 30, 600 min oxidation at 21°C.

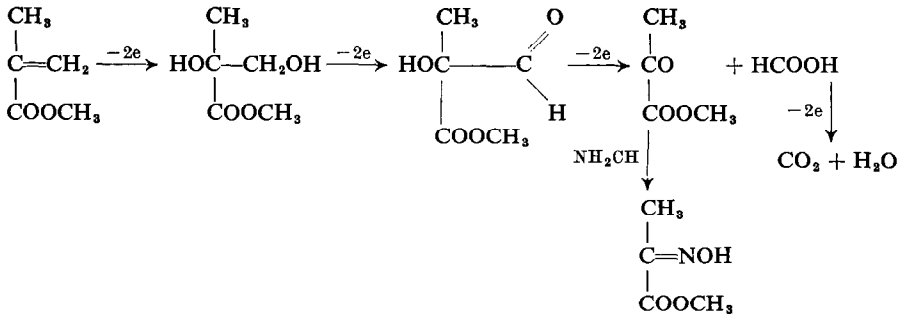
analysis: theoretical—C 41·03%, H 6·03%, N 11·96%; found—C 40·8%, H 6·2%, N 12·3%.

The methyl pyruvate oxime is hence the product which is electro-reduced in the polarographic determination.

From the rate of oxidation of pyruvic acid, methyl methacrylate, methyl lactate and methyl pyruvate (Fig. 1) it is evident that neither methyl lactate nor pyruvic acid is formed in considerable amounts in the course of reaction. Pyruvic acid undergoes rapid and complete oxidation, whereas methyl pyruvate resists further oxidation. This difference in reactivity can be explained in the following manner: the methacrylates

cannot form a complex with manganese(III), the intervention of which is, according to Drummond and Waters,[23] the necessary condition for fission of a double bond. When methyl lactate undergoes quantitative oxidation the velocity of the reaction is much slower.

The oxidation of methyl methacrylate to methyl pyruvate proceeds *via* a compound of which the oxime has a half-wave potential 0·3 V more negative than that of methyl pyruvate oxime (Fig. 2). The sum of the heights of the polarographic waves of this compound and of methyl pyruvate oxime varies during the oxidation only slightly. Hence, both compounds have similar diffusion coefficients, molecular weights and chemical character. It is possible that the methyl ester of 2-hydroxy-2-formylbutyric acid may be this intermediate oxidation product. The suggested reaction scheme is as follows:



The oxidation of other methacrylates (Fig. 3) and acrylates (Fig. 4) follows a similar scheme. From the oxidation of acrylates, glyoxalates result, which undergo further oxidation much more easily than pyruvates. This fact could be a basis for differentiation between pyruvates and glyoxalates or methacrylates and acrylates.

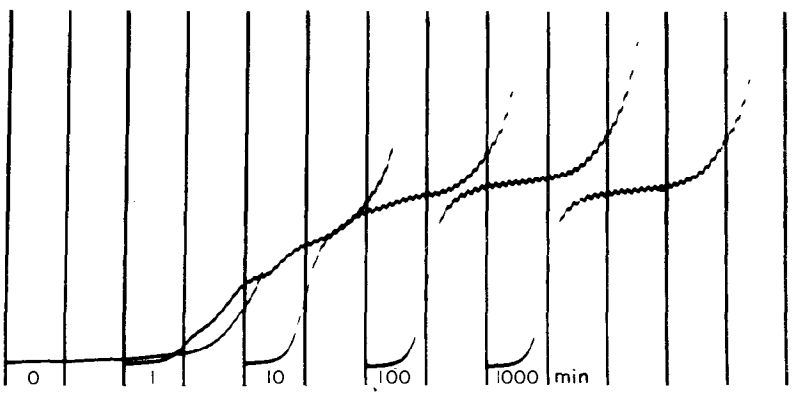


FIG. 3.—Rate of oxidation of butyl methacrylate (0·41 mmole) at 22°C. Conditions as for Fig. 1.

Optimum conditions for oxidation of methyl methacrylate

The time dependence of the effect of different permanganate excesses on methyl methacrylate at different pH values, temperatures and ionic strengths, was studied.

The optimum pH for the oxidation is 2·70 (Fig. 5) or a mineral acid concentration of 0·005*N* (Fig. 6); good results are also given by 0·1*M* acetic acid. The investigation of the rate of reaction (Fig. 7) has shown that in a more acidic solution the reaction is

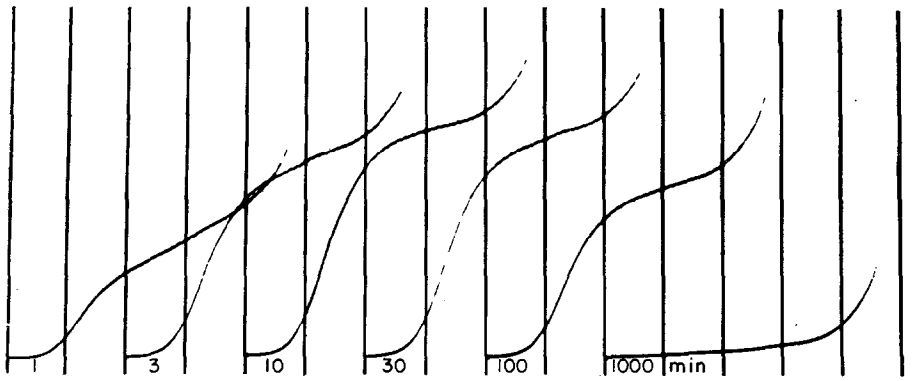


FIG. 4.—Rate of oxidation of methyl acrylate (0·82 mmole) at 22°C.
Conditions as for Fig. 2.

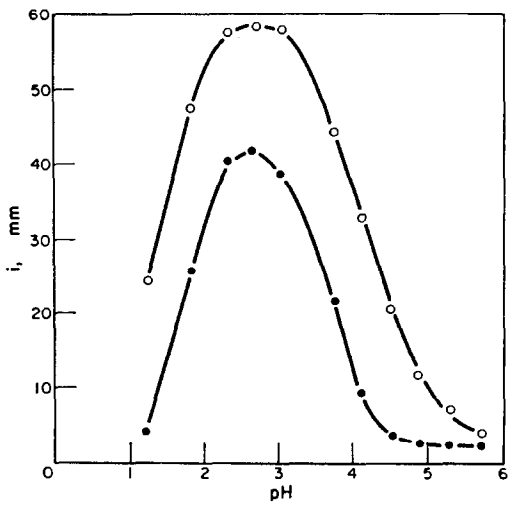


FIG. 5.—Effect of pH on degree of oxidation of methyl methacrylate (0·82 mmole) at 23°C.
The heights of the polarographic waves (sensitivity 1/20) refer to the oximes of the products obtained after 45 (○) and 75 (●) hr oxidation with 0·02*N* permanganate at various pH values. HCl/KCl buffers were used for the range of pH 1·22–3·05, and acetate buffer for pH 3·73–5·71.

not stoichiometric and further oxidation occurs. At higher pH the result is similar.

Excess of permanganate promotes further oxidation (Fig. 8). The investigation of permanganate consumption and its dependence on the volume of the added permanganate shows that the six-electron oxidation that gives rise to methyl pyruvate is followed by the two-electron oxidation of the liberated formic acid to carbon dioxide and water. Whilst the first step of the oxidation is stoichiometric, the second step needs a great excess of permanganate for its completion (Fig. 9).

Increasing the temperature of the reaction mixture accelerates not only the oxidation to the pyruvate but also the further oxidation, which is undesirable analytically (Fig. 10).

The relationship of the temperature and the time required to achieve 97–100%

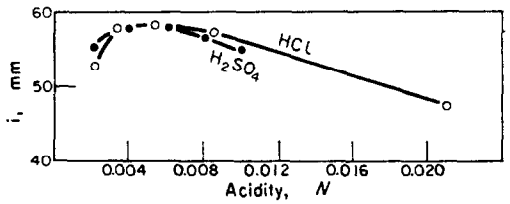


FIG. 6.—Effect of acid concentration on degree of oxidation of methyl methacrylate (0·82 mmole) by treatment with 0·02*N* permanganate for 45 hr at 25°C.

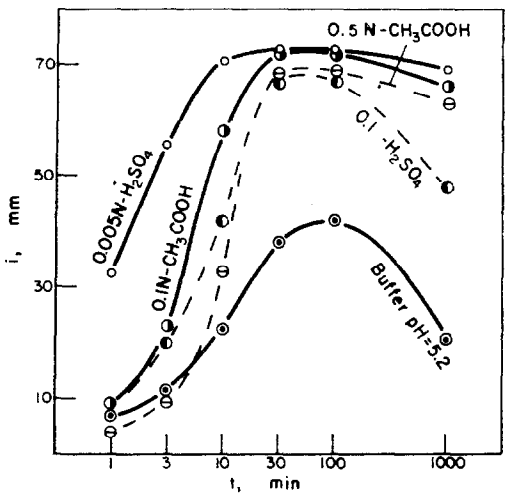


FIG. 7.—Rates of oxidation of methyl methacrylate (0·82 mmole) at 20°C with 0·02*N* permanganate at different acidities.

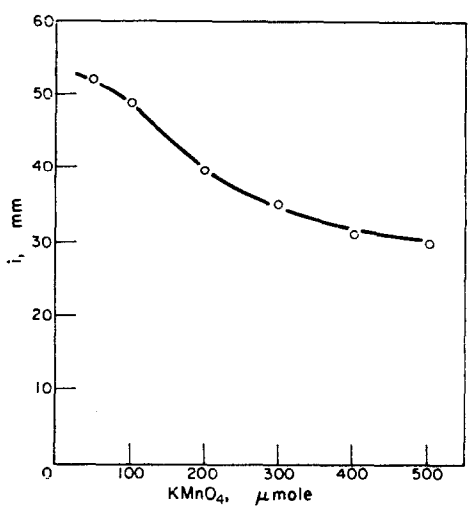


FIG. 8.—Effect of excess of permanganate on degree of oxidation of methyl methacrylate (5 μmole) for 24 hr at 20°C in 0·005*N* sulphuric acid.

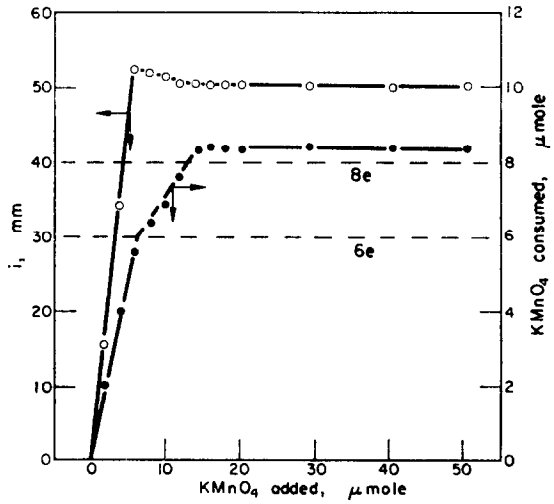


FIG. 9.—Stoichiometry of the oxidation of methyl methacrylate (5 μmole) for 24 hr at 20°C with permanganate in 0·005*N* sulphuric acid.
○—oxime formed (galvanometer sensitivity 1/30),
●—permanganate consumed.

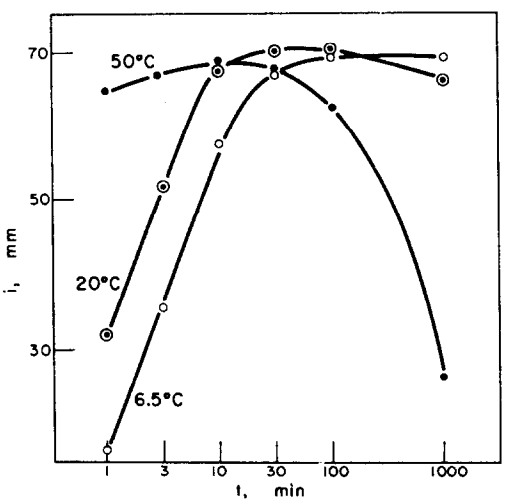


FIG. 10.—Rate of oxidation of methyl methacrylate (0·82 mmole) with 0·02*N* permanganate in 0·005*N* sulphuric acid, at different temperatures.

conversion is presented in Fig. 11. Ionic strength within the range 0·05–0·20 has no effect on the reaction. Higher ionic strength accelerates further oxidation of pyruvate.

Polarographic determination of methyl pyruvate oxime

The determination of pyruvate can be combined with there moval of excess of oxidant. With the aid of hydroxylamine hydrochloride, the excess of permanganate is destroyed and the resulting methyl pyruvate is converted into oxime, which can be determined polarographically. The polarographic determination of pyruvate in the form of oxime is also advantageous, because it is more sensitive than

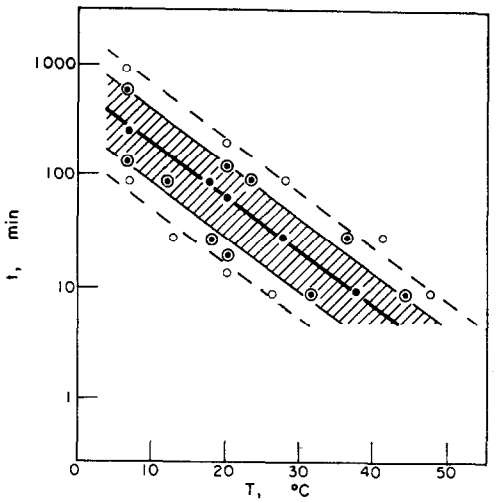


FIG. 11.—Inter-relationship of time and temperature needed for different degrees of oxidation of methyl methacrylate (0·82 mmole) by 0·02*N* permanganate in 0·005*N* sulphuric acid.
○—97%; ⊙—99%; ●—~100%

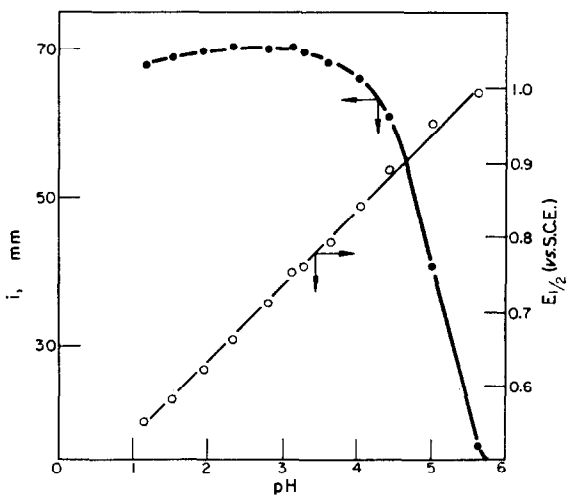
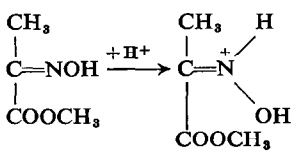


FIG. 12.—Effect of pH on the polarography of the oxime of methyl pyruvate (0·79 mmole).
●—limiting current; ○—half-wave potential. Polarograms were recorded immediately after preparation of the solutions, to avoid errors from hydrolysis of the oxime at pH <2·8.

polarographic determination of the pyruvate alone. While the former compound undergoes a four-electron polarographic reduction, the latter undergoes only a two-electron reduction.

At the dropping mercury electrode, the oxime is easily reduced in the protonated form:[24–26]



Generally, oximes are very weak bases and the pK of their positive ion, according to Brønsted's theory, is less than unity.[25] For this reason, at pH >1, the kinetic current arising from the recombination of the cation contributes considerably to the total height of the polarographic wave. The dependence of the wave height on pH is represented in Fig. 12. At pH 4·4 a more negative polarographic wave appears,

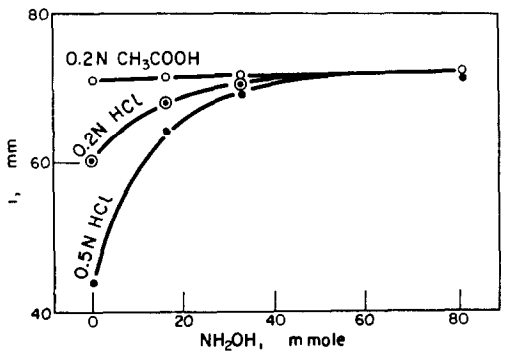


FIG. 13.—Effect of excess of hydroxylamine on limiting current for methyl pyruvate oxime (0·82 mmole) at various acidities.

caused by the reduction of uncharged molecules of the oxime. It is advantageous to work with a strongly acidic solution, where the excess of hydroxylamine does not interfere[26] and the oxime yields a simple diffusion current. To prevent the acid-catalysed hydrolysis of oxime,[26] an excess of hydroxylamine is maintained in the solution (Fig. 13). The maximum on the polarographic wave may be suppressed by gelatin[26] or tylose.[25]

Practical application

The need for a suitable method of determination of methyl methacrylate vapours in air for the purposes of industrial hygiene was the first stimulus for this work. First, it was necessary to seek a suitable method of absorption of methacrylate vapours from the air. The best absorption is given by permanganate solution, because of the immediate oxidation of absorbed ester. For this reason, the permanganate oxidation has been taken as a basis for the method.

Laboratory control of the absorption process was achieved by means of aeration of the ester from a standard solution into two absorption vessels in series. At an aeration velocity of 0·4–1·2 l/min about 3·5% of the total amount of ester passes into the second absorption vessel. At velocities of 0·08–0·20 l/min, an average of 2·8% of the total amount of ester passes into the second absorption vessel.

Interfering substances in this determination include aldehydes and ketones, and alcohols, esters and unsaturated compounds which can produce aldehydes and ketones by oxidation (Table I).

In an oxidation lasting 100 min, the presence of acetaldehyde, benzaldehyde, acetone, ethanol, and esters of acetic acid does not interfere. These compounds can only interfere by consuming some of the permanganate used to oxidize the methacrylate. The interference of acrylates and styrene can be prevented by prolonged oxidation. The oxidation of formaldehyde is very slow and hence it interferes in this determination as also does methanol, from which formaldehyde arises by oxidation.

TABLE I.—INTERFERENCE OF VARIOUS COMPOUNDS IN THE DETERMINATION OF METHYL METHACRYLATE

Compound	Amount, *μmole*	Height of interfering polarographic wave, *mm*, after *x* min oxidation					Interference after *x* min oxidation, %			$EV_{1/2}$,
	x	0	1	10	100	1000	0	100	1000	
Formaldehyde	6·34	10·0	10·0	9·5	8·0	—	15	12	—	0·64 0·89
Acetaldehyde	5·00	0	0	0	0	—	0	0	—	0·83 1·05
Benzaldehyde	5·62	30·5	24·5	8·0	0·5	0	52	0·9	0	0·52
Acetone	5·00	0	0	0	0	—	0	0	—	0·94
Methanol	5·36	0	6·0	6·0	6·0	—	0	11	—	0·70
Ethanol	5·00	0	0	0	0	—	0	0	—	1·00
Ethyl acetate	5·00	0	0	0	0	—	0	0	—	—
Butyl acetate	5·00	0	0	0	0	—	0	0	—	—
Methyl acrylate	5·00	0	26·0	40·5	31·0	2·0	0	60	3·8	0·47
Butyl acrylate	2·50	0	10·0	17·0	14·0	3·0	0	54	11·6	0·34
Styrene	1·13	0	7·0	7·0	4·0	0	0	34	0	0·52
Methyl methacrylate	5·00	0	24·1	50·2	52·0	49·0	0	100	94	0·49
Butyl methacrylate	2·50	0	4·3	19·9	24·5	23·4	0	94	90	0·40

The interference is expressed as a fraction of the height of the polarographic wave for an equal molar concentration of methyl pyruvate oxime. The last column records the values of $E_{1/2}$ (*vs.* S.C.E.) of the polarographic waves of the oxidation products, in the presence of excess of hydroxylamine at pH 0·9.

Recommended procedure for the determination of vapours of methacrylate in air

Absorb the vapours of methacrylate in 5–10 ml of absorption solution (100 ml of 0·1*N* potassium permanganate and 25 ml of 0·1*N* sulphuric acid made up to 500 ml with distilled water) in an absorption vessel fitted with a fritted disc. The sampling velocity is about 1 l/min. If the absorption solution is decolorized during sampling, take a new, smaller, sample. When the sampling is finished, wait 100 min (for temperature 5–28°) and then add 1 ml of reducing solution (2·5% hydroxylamine hydrochloride in 1*M* hydrochloric acid) for every 5 ml of absorption solution. Record the polarographic curve, after the addition of 0·05 ml of 0·5% tylose for every 6 ml of the sample, in an atmosphere of nitrogen, with a saturated calomel electrode, over the range 0·2–1·0 V.

For calibration, use an aqueous solution of freshly distilled methacrylate, oxidized for 100 min with an equal volume of absorption solution containing double the designed amount of potassium permanganate and sulphuric acid.

Alternatively, the methyl pyruvate oxime alone can be used for calibration, dissolved in a mixture of the absorption and reduction solutions (5 + 1).

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Zusammenfassung—Die Oxidation von Methylmethacrylat mit Permanganat in schwach saurer Lösung liefert Methylpyruvat. Zur Zerstörung überschüssigen Permanganats wird Hydroxylaminhydrochlorid verwendet. Gleichzeitig wird es zur Oximierung des Pyruvats verbraucht; das entstandene Oxim wird polarographisch bestimmt. Ein Reaktionsmechanismus für die Permanganatoxidation von Methylmethacrylat wird vorgeschlagen und die optimalen Arbeitsbedingungen für Permanganatoxidation und polarographische Bestimmung angegeben. Die Methode wird zur Bestimmung von Methylmethacrylatdämpfen in der Luft zu industriehygienischen Zwecken verwendet.

Résumé—L'oxydation permanganique du méthacrylate de méthyle en solution faiblement acide donne du pyruvate de méthyle. On utilise le chlorhydrate d'hydroxylamine pour détruire l'excès de permanganate. En même temps, il est consommé pour l'oximation du pyruvate, et l'on dose polarographiquement l'oxime résultante. On suggère le schéma réactionnel de l'oxydation permanganique du méthacrylate de méthyle et l'on a trouvé les conditions de travail optimales tant pour l'oxydation permanganique que pour le dosage polarographique. On utilise la méthode pour le dosage de vapeurs de méthacrylate de méthyle dans l'air, à des fins d'hygiène industrielle.

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SEPARATION OF IONS BY ALTERATION OF THE CONCENTRATION OF THE LIGAND IN A DISCONTINUOUS COUNTERCURRENT EXTRACTION SYSTEM

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Summary—A new technique in Craig-type liquid-liquid, discontinuous, countercurrent solvent extraction was developed. In this, the ligand concentration in the extraction train was altered at several points, causing non-equivalent changes in the extractability of the ions being separated. This allowed quantitative separation of a mixture with a minimum number of transfers, thereby keeping the solvent volume to a minimum. The technique was applied to achieve total or partial separation of a number of elements, using methyl isobutyl ketone as the solvent and hydrochloric acid as the ligand. A computer programme was developed for calculating the distribution of a solute in an extraction train operating under these conditions.

RECENTLY, Craig-type liquid-liquid, discontinuous, countercurrent* solvent extraction has been used for inorganic systems, with applications to geochemical analysis.[1–4] In many cases, good separations of the constituents of solutions of geological materials may be achieved but if the distribution coefficients of constituents between the ligand and solvent are too similar, it is virtually impossible to separate them by countercurrent distribution without an inordinate number of transfers. This difficulty can to some extent be overcome by varying the concentration or nature of the ligand in the lower phase of the extraction train so that there is relative alteration in the extraction characteristics of the species to be separated.[1] For this latter method to be other than empirical, it is necessary to know the extractability of the species and their distribution in the extraction train after a given number of transfers. The former can be obtained experimentally, but although the distribution may also be similarly obtained, it is a time-consuming operation, and there is clearly a place for some method whereby the distribution in the tubes of the extraction train may be calculated. In the case of normal liquid-liquid, discontinuous, countercurrent separation, the distribution can be predicted by the use of tables of the binomial function.[5,6] However, for varying nature or concentration of ligand, no rapid technique for calculating the distribution has hitherto been available.

It is the purpose of this paper to demonstrate further the potentialities of the variable ligand method and to show how a mathematical relationship has been derived from which the theoretical distribution can be calculated. This relationship has been programmed for a computer and has been checked by experimental studies.

* In using the term "countercurrent" for a Craig-type apparatus, we follow accepted practice though realizing that as there is only one moving phase, this term is not strictly correct.

COMPUTATION OF SOLUTE DISTRIBUTION IN AN EXTRACTION TRAIN WITH VARIABLE LIGAND CONCENTRATIONS

The mathematics governing the distribution of a solute in a discontinuous, countercurrent extraction train are relatively simple and lend themselves to the use of high-speed digital computers. This has not hitherto been necessary, owing to the ready availability of extensive tables of the binomial function[7,8] but with systems in which there is an abrupt change in extractability at some stage in the extraction train, these cannot be used.

The amount of material in tube number i after n transfers ($T_{i,n}$) is given by the expression

$$T_{i,n} = A_{i,n-1} + O_{i-1,n-1} \tag{1}$$

where $A_{i,n}$ and $O_{i,n}$ are the amounts of material in the aqueous and organic phases respectively, at equilibrium in tube i after n transfers and are given by

$$A_{i,n} = T_{i,n}\left(\frac{1}{1 + Dr}\right) \tag{2}$$

$$O_{i,n} = T_{i,n}\left(\frac{Dr}{1 + Dr}\right) \tag{3}$$

where D is the distribution coefficient of the solute and r is the ratio of the volumes of the organic and aqueous phases.

If a particular value for the initial amount of solute in the first tube of the extraction train is assumed, a theoretical countercurrent distribution can be evaluated by calculating the amounts in the aqueous and organic phases at equilibrium in each tube, calculating from equation (1) the total amount in each tube after each transfer and then recalculating the amount in the aqueous and organic layers of each tube at equilibrium from equation (2) or (3). The steps outlined above are an arithmetic analogue of the operations of equilibration and transfer followed by a second equilibration.

A programme was written for use on an IBM 1620 computer, utilizing equations (1), (2) and (3) and making it possible to calculate the distribution of a solute in an extraction train in which there are points at which there are abrupt changes in the distribution characteristics of the solute. Copies of the computer programme are available from one of the authors (C. R. Boswell).

EXPERIMENTAL

The extractabilities of a large number of metal ions from hydrochloric acid by methyl isobutyl ketone (MIBK) are known[4] and vary considerably with acid concentration. Using these data, a scheme was devised for separating a number of elements with similar extraction characteristics by altering the conditions on the extraction train.

The system involved the separation or partial separation of gold, zinc, cadmium, mercury, gallium, indium, thallium, tin, lead, arsenic, antimony, bismuth and iron by the use of counter-current distribution. The first 20 tubes of the extraction train contained $7M$ hydrochloric acid, the next 40 tubes contained $2M$ hydrochloric acid and the remaining 10 contained $0{\cdot}5M$ hydrochloric acid. The first tube of the train contained a solution of the elements mentioned, in $6M$ hydrochloric acid. This solution had previously been oxidized with chlorine gas to ensure that all elements were in their highest oxidation states. The organic phase was redistilled MIBK.

Each step of the process involved an equilibration time of 3 min and a settling time of 4 min. Previous work[4] had indicated that these times were sufficient to achieve complete equilibration of the complexes and separation of the phases.

Apparatus

The apparatus used was a 120-tube, fully automatic, discontinuous, countercurrent extraction apparatus. The individual extraction tubes were mounted on a shaking-rack, the axis of which was attached to a control unit which automatically effected the operations of shaking, settling and decantation. Individual tubes had a capacity of 20 ml for the stationary lower phase and the moving upper phase was fed into the system at the end of each cycle by means of a 20-ml dispenser attached to a 10-l. reservoir. After each shaking operation, the rack was tilted through 90° and the upper phase decanted into the next tube.

Procedure

All acid used was pre-equilibrated with MIBK. The solvent, which had been pre-equilibrated with 6*M* hydrochloric acid, was fed into the system from the reservoir, and countercurrent extraction was carried out for 70 transfers. The contents of pairs of tubes were evaporated to dryness, sodium chloride was added as carrier, and the residues were examined spectrographically in a d.c. arc, with anode excitation. All spectra were recorded on one photographic plate and the distribution of any element was found by visual observation of a sensitive spectral line of that element. Densitometric measurements were not necessary except in cases of doubt.

RESULTS AND DISCUSSION

The results are shown in Fig. 1 together with the theoretical distributions as calculated from the computer programme. In the calculations, allowance was made

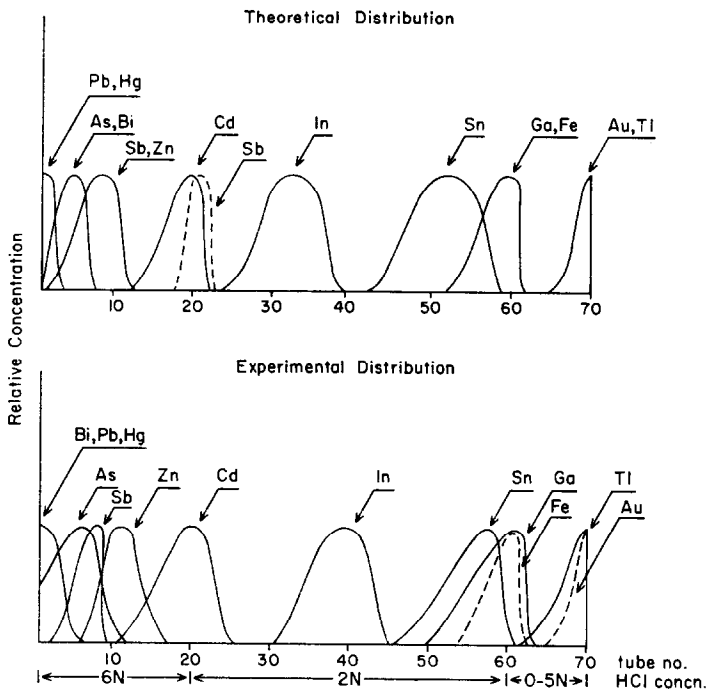

FIG. 1.—Theoretical and experimental distribution curves for certain elements after countercurrent extraction with methylisobutyl ketone with varying concentrations of hydrochloric acid in the aqueous phase.

for the two oxidation states of antimony. In the experimental work, only the peak corresponding to the species with lower extraction was found. The distribution patterns of indium and tin are displaced further along the train than expected from calculations. This is most probably due to the fact that after the solvent front, saturated with 6*M* acid, reached tube number 20, redistribution of the acid between

the two phases occurred with a consequent rise in acid concentration in the first tubes originally containing the 2*M* acid and a corresponding change in the extraction characteristics of these elements. In view of this, the agreement between the experimental and calculated distributions is very satisfactory and would indicate that movements of acid are relatively insignificant.

The results have shown that liquid-liquid, discontinuous countercurrent extraction systems in which conditions on the extraction train are altered at various stages are particularly useful in separating multicomponent mixtures, especially where the optimum conditions for separating certain components are not those for separating other components. In the case considered here, it is possible to separate quantitatively a mixture of lead, cadmium, indium, iron and gold, with only 70 equilibration stages. If the conventional system were used, a much greater number of equilibration stages would be necessary and it is doubtful whether even then a satisfactory separation of iron and gold would be attained. The saving of time and economy in solvent volume when the modified technique is used are obvious.

Acknowledgements—The authors are indebted to the New Zealand University Research Committee and the Nuffield Foundation for grants towards the establishment of a spectrographic laboratory at Massey University. They are also grateful to Chemistry Division, D.S.I.R. for the loan of a 120-tube, discontinuous, countercurrent extraction apparatus.

Zusammenfassung—Eine neue Arbeitsweise bei der diskontinuierlichen Gegenstromextraktion nach Craig wurde entwickelt. Dabei wird die Ligandenkonzentration in der Extraktionsbatterie an mehreren Punkten geändert, wobei sich ungleiche Änderungen in der Extrahierbarkeit der zu trennenden Ionen ergeben. Damit wurde quantitative Trennung einer Mischung mit einer Mindestzahl von Schritten erreicht, wobei das Lösungsmittelvolumen am Minimum gehalten wird. Das Verfahren wurde zur totalen oder teilweisen Trennung einer Reihe von Elementen mit Methylisobutylketon als Lösungsmittel und Salzsäure als Ligand verwendet. Ein Rechenprogramm zur Berechnung der Verteilung eines gelösten Stoffes auf eine unter den angegebenen Bedingungen arbeitende Extraktionsbatterie wurde erstellt.

Résumé—On a élaboré une nouvelle technique d'extraction discontinue à contre-courant, par solvant, en phase liquide, du type Craig. Dans celle-ci, la concentration en ligand dans l'ensemble d'extraction a été modifiée en différents points, causant des changements non équivalents dans l'extractibilité des ions à séparer. Ceci a permis une séparation quantitative d'un mélange avec un nombre minimal de transferts, maintenant de ce fait le volume de solvant à un minimum. On a appliqué la technique pour effectuer la séparation totale ou partielle d'un certain nombre d'éléments en utilisant la méthylisobutylcétone comme solvant et l'acide chlorhydrique comme ligand. On a élaboré un programme de computation pour calculer la distribution d'un soluté dans un ensemble d'extraction opérant dans les conditions ci-dessus.

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EXTRACTION OF ANTIMONY WITH TERTIARY AMINES

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Summary—The extractability of antimony(III) and (V) with tridodecylamine from various aqueous solutions is reported. Extraction from nitric and hydrofluoric acid solutions is low, but extraction from sulphuric, hydrochloric and hydrobromic solutions is high. Antimony(III) can be separated from antimony(V) in 7*M* nitric acid or 0·64*M* hydrobromic acid. The extraction of antimony from hydrochloric acid solutions in methanol, ethanol, and acetone–water mixtures is greater than from pure aqueous solutions of the same acidity. The elements from which antimony can be separated with tertiary amines are given.

THE extraction of antimony with different organic solvents has been investigated by many authors.[1,2] The solvents studied include ethyl acetate benzene, alcohols and ethers,[3,4] organo-phosphorus solvents[5] and others.[6–10] Conditions have been determined for the isolation of antimony from other elements by these solvents and the nature of the extraction processes has also been examined.

Amine extraction of the elements has attracted the attention of chemists in the past few years because of the availability of such solvents and their high stability and selectivity, and has been well reviewed.[11,12] An analogy between extraction with amines and anion-exchange on solid resins has often been drawn. In earlier studies from this laboratory the extraction of cerium, thorium, uranium, neptunium and zirconium with tertiary amines has been investigated and the stability constants of the extraction reactions have been determined.[13–16]

The aim of the present work was to carry out a systematic study on the extractability of antimony in its two oxidation states from various acidic media with tertiary amines, and to explain the mechanism of extraction. The extraction of some other elements was also studied in order to determine the elements from which antimony can be selectively isolated with tertiary amines.

EXPERIMENTAL

Apparatus

Scintillation counter. EKCO with well crystal NaI(Tl) type.

Reagents

Antimony solutions. A mixture of antimony-122 and antimony-124 was obtained by irradiating metallic antimony of high purity in the UA-RR-1 2MW Research reactor at Inshas for 48 hr. Approximately 30 mg of irradiated antimony were dissolved by heating with the minimum amount of concentrated sulphuric acid till dissolution was complete. The solution was then heated to fumes and subsequently diluted with 6*M* hydrochloric acid. This was the stock solution of radioactive antimony(III). A stock solution of radioactive antimony(V) was prepared by heating a similar amount of irradiated antimony with a mixture of concentrated sulphuric acid and nitric acid (1 + 1) till dissolution was complete. The solution was heated till fuming and then cooled and diluted with 6*M*

hydrochloric acid. Carrier solutions of antimony(III) (0·0128*M*) and antimony(V) (0·144*M*) were prepared by dissolving suitable amounts of unirradiated metallic antimony in a similar manner.

Other ions. Suitable isotopes of iron, zinc, cobalt, silver, mercury, zirconium, scandium, cerium, caesium and chromium were obtained by irradiation. Protactinium-233 was prepared by dissolving about 5 mg of irradiated pure thorium nitrate in about 5 ml of 5*M* hydrochloric acid–1*M* lithium chloride solution, and then extracting with an equal volume of 0·3*M* trioctyl amine in benzene. Protactinium-233 was then re-extracted from the organic phase with 5 ml of 1·5*M* hydrochloric acid, and this aqueous solution was mixed with an equal volume of concentrated hydrochloric acid. The final volume of each tracer solution was selected so that 50 μl diluted to 5 ml had a measured activity of 5000–75,000 cpm.

Amine. Trilaurylamine or tridodecylamine (TDA), a high purity product of Rhone-poulenc, France, was used as a typical long-chain tertiary amine in the present study, without further purification.

Solvents. The diluents used were reagent grade xylene, toluene and benzene, and Egyptian "Sunrise" odourless kerosene.

Other chemicals and reagents were of the highest purity available.

Determination of distribution ratio

Extraction experiments were carried out by mixing 5 ml of the organic phase with 5 ml of aqueous phase to which 50 μl of tracer solution had been added, and shaking the mixture at room temperature (21 $\pm$ 4°) for about 1 hr. The layers were separated by centrifugation. Preliminary experiments showed that fluctuations of the temperature of the order indicated have no significant effect on the distribution ratios and that equilibrium is always reached in less than 1 hr. The distribution was determined by measuring the radioactivity of 3-ml aliquots of both phases after equilibration. The amine was always pre-equilibrated with acid of appropriate concentration. The concentration of acid in the aqueous solution left after extraction was determined by titration with sodium hydroxide solution. The distribution ratio (*E*) was taken to be the ratio of the activities of the tracer in the organic and aqueous phases. Because of the high reproducibility of the results, determinations were only carried out in duplicate.

RESULTS AND DISCUSSION

Extraction of antimony with xylene from nitric, hydrochloric and sulphuric acid media

The distribution of antimony between xylene and aqueous solutions of nitric, hydrochloric, and sulphuric acid was investigated. The results are shown in Table I.

TABLE I.—EFFECT OF ACIDITY ON *E* FOR Sb(III) AND Sb(V) EXTRACTED WITH XYLENE

Acid	*M*	*E*	
		Sb(III)*	Sb(V)*
HNO_3	1·5–15	No extraction	No extraction
H_2SO_4	1·8	0·0129	0·0096
	5·4	2·09	0·022
	10·8	2·05	0·63
	12·6	24·1	10·8
	18·0	75·0	20·7
HCl	2·4	0·0161	0·003
	3·6	0·0172	0·006
	6·0	0·0219	0·024
	8·4	0·05	0·08
	12·0	0·124	0·27

* Tracer antimony concentration.

Extraction of antimony with TDA from nitric acid

The extraction of antimony from nitric acid solutions of various concentrations has been studied for different concentrations of amine. The experimental values of *E* for

0·06*M* TDA are shown in Fig. 1. It is evident that antimony(III) is extracted much better than antimony(V). The maximum extraction of antimony(III) occurs from 8*M* nitric acid. This behaviour is identical with that for thorium, cerium(III), uranium(VI) and neptunium(IV) and (VI), and can thus be described as an anion-exchange partition:

$$m\mathrm{R_3NHX} + (m+n)\mathrm{MX}^{-m} \rightleftharpoons (\mathrm{R_3NH})_m\mathrm{MX}_{(m+n)} + m\mathrm{X}^- . \quad (1)$$

Such partition may alternatively be regarded as adduct formation between a neutral complex and the amine salt:

$$m\mathrm{R_3NHX} + \mathrm{MX_n} \rightleftharpoons (\mathrm{R_3NH})_m\mathrm{MX}_{(m+n)}. \quad (2)$$

The two equations are thermodynamically equivalent.[12]

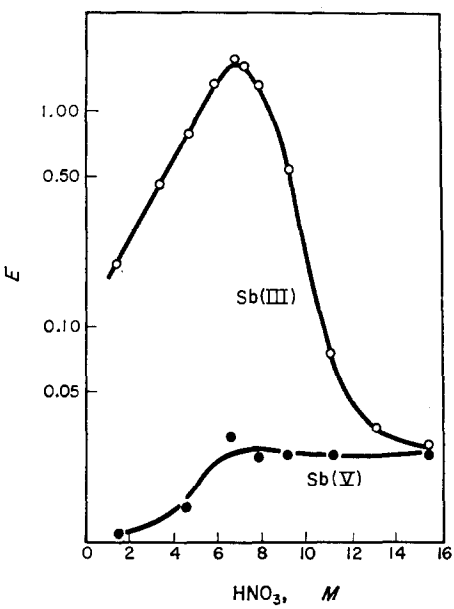

FIG. 1.—Effect of nitric acid concentration on *E* extracted by 0·06*M* TDA in xylene.

Accordingly the increase of antimony extraction with increasing nitric acid concentration can be explained by the salting out effect of the nitrate ion, while the subsequent decrease can be related either to anion competition for the available amine, or to the formation of an amine dinitrate, $\mathrm{R_3N(HNO_3)_2}$,[17] assuming that this does not interact with the metal nitrate.[12]

Such partition has been verified experimentally for the other elements and on the basis of the solvate numbers (*m*), obtained, the values of the extraction constants have been estimated.[13,14,18–20]

The decrease in *E* with increase in acid concentration is greater for antimony(III), than for the other elements mentioned. This can be attributed to the partial oxidation of antimony(III) to the less extractable antimony(V) at high nitric acid concentrations. In favour of this view is the fact that the extraction of the two oxidation states becomes the same from $\sim 15M$ nitric acid, when the oxidation is complete (Fig. 1). This interpretation was confirmed by letting antimony(III) stand with 15*M* nitric acid for about 1 hr and then determining its extractability at various nitric acid

concentrations; the values of E obtained were identical with those obtained with antimony(V).

It is clear that antimony(III) and (V) may be separated from each other by extraction of the former from about 7M nitric acid.

The values of E as a function of amine concentration for antimony(III) (Table II) did not indicate any definite extraction stoichiometry. A log–log plot of E *vs.* amine concentration for antimony(V) gives a straight line with a slope of about 1 (Fig. 2), suggesting an extractable antimony(V) complex in which the metal : amine ratio is 1 : 1.

TABLE II.—EFFECT OF AMINE NITRATE CONCENTRATION ON E OF ANTIMONY(III) FROM 4·8M NITRIC ACID

TDA, M	E
0·006	0·674
0·012	0·774
0·024	0·652
0·042	0·510
0·150	0·423

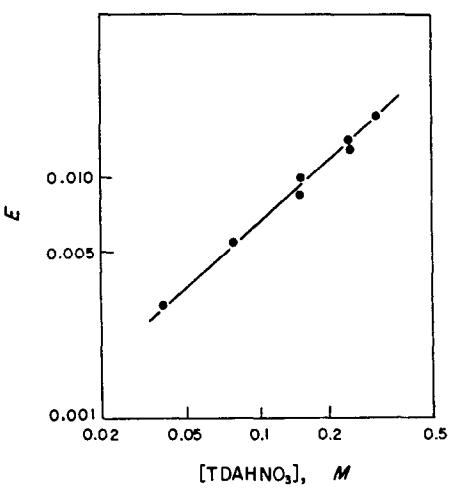

FIG. 2.—Effect of [TDA.HNO_3] on E of Sb(V) [HNO_3] = 8M.

Extraction of antimony from sulphuric acid

Both antimony(III) and (V) sulphates are efficiently extracted by TDA (Fig. 3). The extraction is much greater than with pure xylene or from nitrate medium, indicating that the amine sulphate complexes of antimony are much more stable than the amine nitrate complexes. The presence of maxima in the partition curves may be explained in the same way as for nitrate extraction.

Results on the effect of the amine sulphate concentration on E are given in Table III. No conclusions regarding the extraction mechanism can be made from these results, because both oxidation states are considerably extracted with pure xylene. The absence of extraction stoichiometry may also be related to the non-ideality of the organic phase.[12]

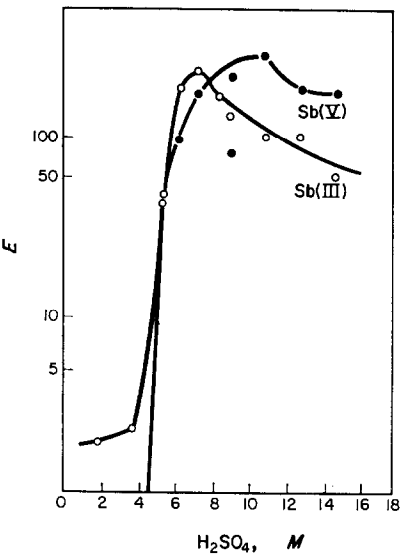

FIG. 3.—Effect of sulphuric acid concentration on E 0·06M TDA in xylene.

TABLE III.—EFFECT OF AMINE SULPHATE CONCENTRATION ON E FOR Sb(III) AND Sb(V)

TDA, M	E	
	Sb(III)*	Sb(V)†
0·006	1·515	78·75
0·012	1·850	35·0
0·024	1·925	34·7
0·042	2·45	87·5
0·150	3·17	128·3

* Aqueous phase: tracer antimony in 3·6M H_2SO_4.
† Aqueous phase: tracer antimony in 5·4M H_2SO_4.

Extraction of antimony from hydrochloric acid

The distribution of antimony(III) and (V) as a function of hydrochloric acid concentration at fixed TDA concentration (0·06M) has been determined (Fig. 4). Maximum extraction is obtained at $\sim$ 5M hydrochloric acid for antimony(III) and at $\sim$ 7M hydrochloric acid for antimony(V). The decrease of E at higher acid molarities can be related, as with nitrate and sulphate extraction, to the formation of amine polychlorides; the formation of $R_3N(HCl)_2$ has been supported by infrared absorption[21,22] and nuclear magnetic resonance measurements.[23]

Log-log plots of E *vs.* [TDA,HCl] give straight lines with slopes of about 1 for antimony(III) and (V) (Fig. 5). This suggests the extraction of antimony monoamine complexes, $TDAH{\cdot}SBCl_4$ and $TDAH{\cdot}SbCl_6$; the formation of $[SbCl_4]^-$ and $[SbCl_6]^-$ complexes has been reported for antimony in chloride medium.[12]

The extraction of antimony chlorides has been also studied as a function of the initial metal concentration in the aqueous solution. The mean E values for extraction from 4·8 and 5·8M hydrochloric acid are shown in Tables IV and V.

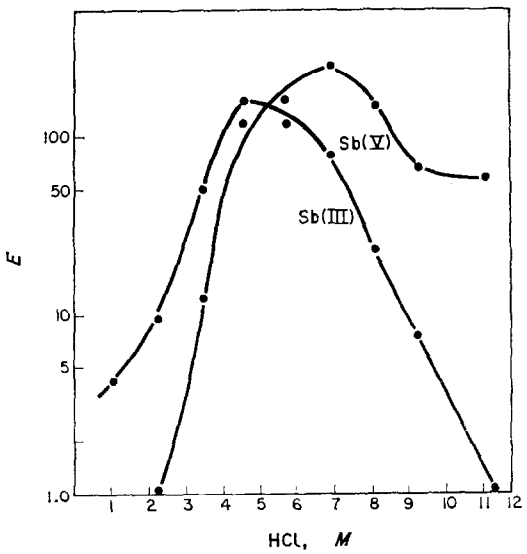

FIG. 4.—Effect of hydrochloric acid concentration on E
0·06M TDA in xylene.

For low amine concentrations the values of E decrease with increasing antimony concentration because of the decrease of the free amine concentration, while for high amine molarities extraction is almost constant and quantitative for all metal concentrations over the range studied.

Extraction of antimony from hydrobromic and hydrofluoric acids

Distribution ratios for the extraction of antimony from solutions of hydrobromic and hydrofluoric acids of varying molarity in the presence of a constant concentration of TDA are shown in Tables VI and VII.

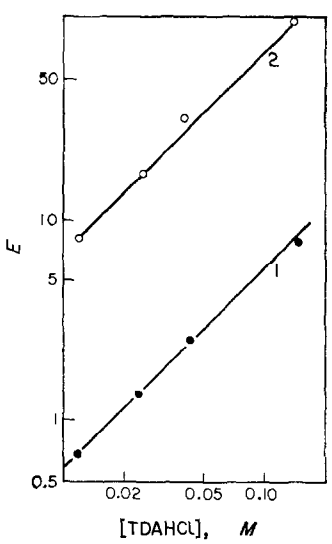

FIG. 5.—Effect of [TDA.HCl] on E
1. Sb(V); 3M HCl
2. Sb(III); 3M HCl.

TABLE IV.—EFFECT OF Sb(III) CONCENTRATION ON ITS EXTRACTION WITH TDA

Initial [Sb(III)], M	E	
	0·06M TDA*	0·3M TDA*
0·0064	67	200
0·0128	59	200
0·0192	40	200
0·0320	12	200
0·0448	5·5	200
0·0640	2·6	200

* Initial HCl concentration 5·8M.

TABLE V.—EFFECT OF Sb(V) CONCENTRATION ON ITS EXTRACTION WITH TDA

Initial [Sb(V)], M	E	
	0·06M TDA*	0·3M TDA*
0·0072	>200	185
0·0144	>200	>200
0·0216	196	>200
0·0360	5·0	>200
0·0504	1·9	>200
0·0724	1·0	182

* Initial HCl concentration = 4·8M.

TABLE VI.—EFFECT OF HBr MOLARITY ON E

[HBr] in the original solution, M*	E	
	Sb(III)	Sb(V)
0·64	2·6	0·02
1·60	3·5	0·06
3·20	90	66
3·84	55	41
5·12	26	25
6·06	18	18
6·40	12	12

* TDA, 0·06M.

TABLE VII.—EFFECT OF HF MOLARITY ON E

[HF] in the original solution, M*	E	
	Sb(III)	Sb(V)
0·61	0·21	0·47
1·53	0·18	0·31
3·05	0·12	0·22
3·66	0·12	0·20
4·88	0·13	0·22
5·49	0·13	0·19
6·10	0·16	0·15

* TDA, 0·06M.

Both antimony(III) and (V) are extracted efficiently from solutions of medium concentrations of hydrobromic acid. The extraction of both oxidation states becomes the same at high concentrations of hydrobromic acid; this is probably due to the reduction of antimony(V) to antimony(III) by hydrobromic acid. Antimony(III) and (V) may be separated by the selective extraction of antimony(III) from 0·64*M* hydrobromic acid. Antimony is extracted from hydrofluoric acid to a much lower extent, so that antimony extracted from other media may be back-extracted from the organic phase with hydrofluoric acid.

Effect of the type of diluent on the extraction of antimony

Benzene, toluene or kerosene can be used interchangeably as diluents, except for the extraction of antimony(III) from nitric acid medium (Table VIII). The slight changes in the values of E can be attributed to the differences in the values of the constants of the extraction reactions for the various diluents.[14]

TABLE VIII.—EXTRACTION OF Sb(III) AND Sb(V) WITH 0·3*M* TDA SOLUTIONS IN DIFFERENT DILUENTS

Oxidation state	Aqueous phase	Diluent	E
Sb(III)	4·8*M* HNO_3	benzene	0·46
		toluene	0·73
		kerosene	0·90
	3·6*M* H_2SO_4	benzene	4·7
		toluene	5·0
		kerosene	4·8
	2·4*M* HCl	benzene	24
		toluene	25
		kerosene	organic phase solidifies
Sb(V)	4·8*M* HNO_3	benzene	0·008
		toluene	0·011
		kerosene	0·008
	5·4*M* H_2SO_4	benzene	23·9
		toluene	29·2
		kerosene	27·0
	3·6*M* HCl	benzene	63·4
		toluene	66·2
		kerosene	organic phase solidifies

Effect of water-miscible organic additives on the extraction of antimony

The effect of organic additives on the extraction of antimony(V) from 1·5 *M* hydrochloric acid has been studied. These additives affected the extraction to varying degrees. Thus, E increases with increasing concentration of acetone, methanol and ethanol, whilst it decreases with increasing concentration of butanol (Fig. 6). A possible explanation of these effects is that there is a decrease in hydration as the mole fraction of water decreases and that this is accompanied by an increase in the formation of negatively charged chloride complexes of antimony *e.g.* $SbCl_6^-$. This should bring about an increase in extractability as can be seen from equation (2).

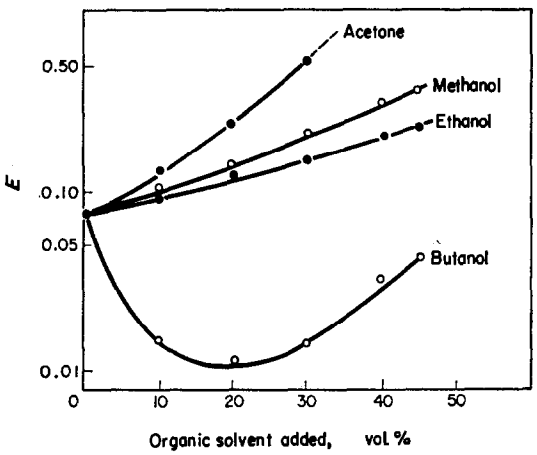

FIG. 6.—Effect of organic additives on E of Sb(V) 1·5M HCl.

TABLE IX.—EFFECT OF METHANOL ON E OF Sb(V)

Original [HCl] in aqueous phase, M*	[Methanol] in aqueous phase, % v/v	E
1·5	—	0·058
	50	0·52
1·8	—	0·14
	40	0·777
2·40	—	0·68
	20	3·38
2·55	—	1·06
	15	4·28
2·70	—	1·58
	10	5·95
2·85	—	2·55
	5	8·50

* TDA, 0·06M in xylene. Trace amounts of antimony.

In the case of butanol the volumes of both phases change during equilibrium because of the solubility of butanol in xylene.

From the results in Table IX it is clear that the addition of methanol in various proportions to the aqueous phase brings about a considerable increase of E.

Separation of antimony from other elements by amine extraction

The highly extractable metal nitrates such as those of uranium, thorium, neptunium and plutonium[18–20] can be easily separated from antimony(V) by extracting them with amines from nitric acid medium.

Both antimony(III) and (VI) are well extracted from sulphate, chloride and bromide media. In this part of study the extraction of a number of some other elements from a chloride medium has been investigated in order to evaluate the selectivity of amine extraction of antimony. The experimental results are presented in Table X. Appropriate radio-isotopes were used to determine E for these elements.

TABLE X.—DISTRIBUTION RATIOS OF SEVERAL ELEMENTS EXTRACTED FROM CHLORIDE MEDIUM*

[HCl], *M*	1·5	3	6	9	12	1·5†
Sb(III)	6·5	31	100	10·8	0·6	>100
Sb(V)	0·4	6·2	>100	95	78	>100
Fe(III)	12	19	57	82	23	>100
Zn	>100	>100	>100	48	1·2	>100
Co	0·01	0·01	0·02	10	0·9	3·5
Pa	0·01	0·8	>100	>100	>100	>100
Se	0·1	0·1	1·7	10	7	42
Ag	42	8·4	0·7	0·1	0·01	>100
Hg	>100	95	70	65	70	>100
Zr	0·05	—	—	—	—	—
Sc, Ce(III) Cs, Cr(III)	no extraction					

* 0·075*M* TDA in xylene. Tracer metal concentration.
† Plus 2·5*M* $AlCl_3$.

From Table X it is evident that antimony, iron(III), zinc, cobalt, hafnium, protactinium, selenium, silver and mercury are well extracted with amine chlorides from 1·5*M* hydrochloric acid–2·5*M* aluminium chloride mixture. These elements can thus be extracted and separated from scandium, chromium, alkali metals, and the rare earths. Silver may be back-extracted from the organic phase with 9*M* hydrochloric acid, then cobalt with 6*M* hydrochloric acid and so on. Antimony may be stripped from the organic phase with 2–4*M* nitric acid containing a few drops of hydrogen peroxide solution as an oxidizing agent or with 3–6*M* hydrofluoric acid.

Zusammenfassung—Über die Extrahierbarkeit von Antimon(III) und -(V) mit Tridodecylamin aus verschiedenen wäßrigen Lösungen wird berichtet. Die Extraktion aus salpeter- und flußsauren Lösungen ist gering, gut jedoch aus schwefelsauren, salzsauren und bromwasserstoffsauren Lösungen. Antimon(III) kann in 7*M* Salpetersäure oder 0,64*M* Bromwasserstoffsäure von Antimon(V) getrennt werden. Die Extraktion von Antimon aus salzsauren Lösungen in Methanol, Äthanol oder Aceton-Wasser-Mischungen ist stärker als aus rein wäßrigen Lösungen derselben Acidität. Die Elemente werden angegeben, von denen Antimon mit tertiären Aminen getrennt werden kann.

Résumé—On décrit l'extractibilité de l'antimoine (III) et (V) au moyen de tridodécylamine à partir de diverses solutions aqueuses. L'extraction est faible à partir de solutions dans les acides nitrique et fluorhydrique, mais elle est élevée à partir de solutions sulfuriques, chlorhydriques et bromhydriques. On peut séparer l'antimoine (III) de l'antimoine (V) en acide nitrique 7*M* ou acide bromhydrique 0,64*M*. L'extraction de l'antimoine à partir de solutions chlorhydriques dans des mélanges méthanol, éthanol et acétone-eau est plus élevée qu'a partir de solutions aqueuses pures de même acidité. On donne les éléments dont on peut séparer l'antimoine au moyen d'amines tertiaires.

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SPECTROPHOTOMETRIC DETERMINATION OF MICRO-AMOUNTS OF VANADIUM WITH 5,7-DI-IODO-8-HYDROXYQUINOLINE

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Summary—A precise spectrophotometric method for the determination of 2·5–25 μg of vanadium in volumes of up to 500 ml of water was developed. The method is based on the simultaneous concentration (100–1000 fold) and complexation of vanadium(V) with di-iodo-oxine in a water-immiscible phase. Interference from iron is eliminated by masking with phosphoric acid. The standard deviation evaluated was $\pm$0·04 μg for solutions containing 5 μg vanadium.

VANADIUM is one of the elements present in trace amounts in plant tissues, biological materials and soil. In plant tissues the amount of vanadium is so minute that Jackson[1] does not mention it. Mitchell *et al.*[2] and Shimp *et al.*[3] have recommended preconcentration with 8-hydroxyquinoline for the spectrochemical analysis of vanadium in soils and biological materials. Although there exist a great number of gravimetric, spectrophotometric, spectrographic and colorimetric microdetermination methods for vanadium using 8-hydroxyquinoline[4] or benzohydroxamic acid[5] as a complexing agent, a method combining concentration of minute amounts from very dilute solutions with highly sensitive determination would be of great advantage. In these methods tervalent iron interferes and has to be separated previously.

5,7-Di-iodo-8-hydroxyquinoline (di-iodo-oxine) is known to be a very sensitive reagent for the gravimetric[6] and heterometric[7] determination of vanadium. The blue-green water-insoluble vanadium di-iodo-oxine complex formed when an acetone solution of the reagent is added to an acidified vanadium solution is readily soluble in organic (water-immiscible) solvents, giving intensely coloured solutions. The colour of these solutions varies from green in chloroform to purple red in higher alcohols.

The principle of the present method is to dissolve the reagent directly in a water-immiscible organic solvent and make use of this solution simultaneously as extractant and complexing agent for vanadium.

EXPERIMENTAL

Instruments

Spectrophotometric measurements were carried out on a Perkin–Elmer Model 137 UV spectrophotometer. All the other photometric measurements were taken at the appropriate wavelength on a Beckman Model B spectrophotometer.

Reagents

An approximately 0·2% solution of 5,7-di-iodo-8-hydroxyquinoline in n-heptyl alcohol was prepared by shaking the reagent mixture for 1 hr, the undissolved reagent then being filtered off. This solution was kept in brown bottles. An aqueous solution of ammonium metavanadate was used. All the other reagents were of analytical grade. Deionized or triply distilled water was used in all experiments.

Procedure

To 500 ml of a neutral solution of vanadium(V), 4*M* phosphoric acid is added to reach the acid concentration of about 0·1*M*. If the solution also contains iron, 3 ml of 4*M* phosphoric acid are needed in addition for every 2–3 mg of iron present. Then 5 ml of the reagent solution are added (the volume needed for complete reaction with 2·5–25 μg of vanadium). The mixture is then shaken for 1 hr to ensure the complete extraction of vanadium. The phases are allowed to separate in a separating funnel and the absorbance of the pink organic extract is measured directly in 10-mm cells at 420 or 475 mμ. The measurements should be taken the same day, since fading was observed after 24 hr.

RESULTS AND DISCUSSION

The choice of the organic solvent

Di-iodo-oxine is insoluble in water and mineral solvents, but slightly soluble in organic solvents. In organic solvents the solubility order chloroform > xylene > amyl acetate > amyl alcohol > n-hexyl alcohol $\simeq$ n-heptyl alcohol > octyl alcohol was observed.

Although it would have been preferable to choose a solvent in which more concentrated reagent solutions could be prepared, this was not possible for the following reasons. Solutions of di-iodo-oxine in chloroform, amyl acetate and xylene are not stable. Chloroform solutions become pink in a few hours, and the colour deepens within a few days to dark red-brown, because of decomposition of the reagent and the liberation of iodine. The colour changes are less pronounced for xylene and amyl acetate but still occur. Amyl alcohol solutions show only a slight yellow colour, but the solvent is slightly miscible with water. Thus, when vanadium is extracted from very dilute solutions (2–5 μg of vanadium in 500 ml of aqueous solution) for which the volume of extractant should be 5–10 ml, practically no phase separation was obtainable.

n-Heptyl alcohol was chosen as the best solvent, being the least water-miscible (the volume of reagent remaining after equilibration of 5 ml of reagent and 500 ml of aqueous phase was about 4·5 ml) and also because no change of colour in the reagent was obtained even after a few weeks. This solvent is preferred to n-hexyl alcohol, mainly because of its less pronounced odour.

Choice of wavelength

Di-iodo-oxine solutions in n-heptyl alcohol have a maximum absorption at 355 mμ (Fig. 1), while in the region of 410–500 mμ, where the vanadium complex absorbs, their absorbance is negligible. This region can be used for the measurements of the vanadium complex. Optimum measurements may be carried out at 420 mμ, since at this wavelength the absorbance is about 30% higher than at 475 mμ. The molar absorptivity calculated from the measurements at 420 mμ was 6000 and that at 475 mμ was about 4800. At both wavelengths the Beer-Lambert law is obeyed for 2·5–25 μg of vanadium. For less than 2·5 μg of vanadium (0·5 μg/ml of extractant) absorbances are too low for accurate reading. If the solution contains more than 25 μg of vanadium the absorbance is too high, and an appropriate dilution is recommended. The standard deviation (20 measurements) was $\pm$0·04 μg for solutions containing 5 μg of vanadium.

The influence of the acid and its concentration

Hydrochloric, orthophosphoric and monochloroacetic acids at various concentrations were studied to establish the optimum working conditions. The results

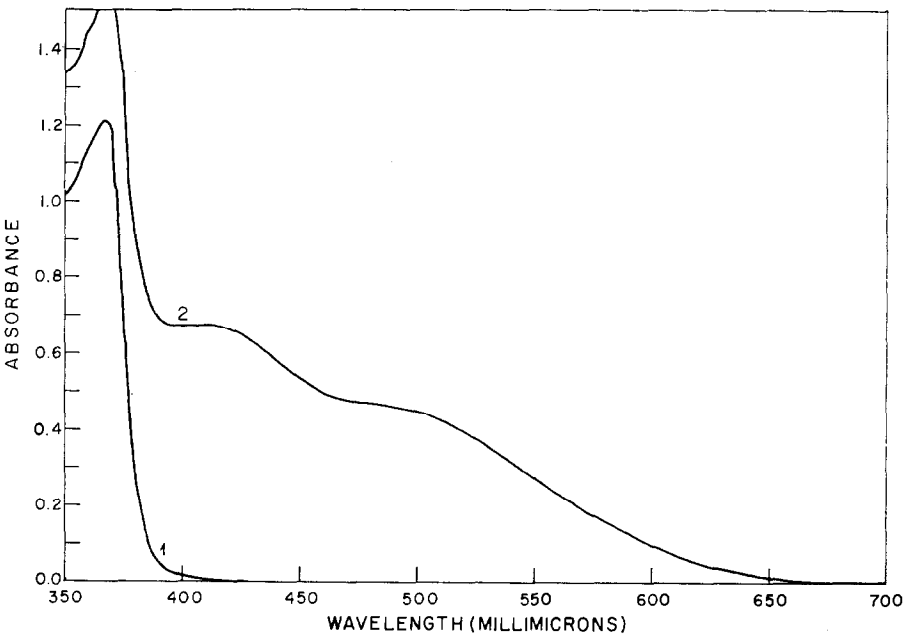

FIG. 1.—Absorption spectra of (1) di-iodo-oxine in n-heptyl-alcohol, (2) vanadium di-iodo-oxine complex in n-heptyl-alcohol.

obtained showed that both the type and concentration of the acid influence the absorbance of the complex solutions. For each acid there is an optimum concentration at which the highest absorbance of the vanadium-di-iodo-oxine complex is obtained. Above and below this concentration, the absorbance is markedly reduced. Optimum results, as may be seen from Table I, were obtained for hydrochloric acid concentration of 0·1*M*.

Extraction time

The first experiments were done with manual shaking of the mixture of vanadium and reagent solutions. It was observed that extraction was incomplete by this method,

TABLE I.—INFLUENCE OF THE ACID AND ITS CONCENTRATION ON THE ABSORBANCE OF 5 μg OF VANADIUM AS ITS DI-IODO-OXINE COMPLEX IN SOLUTIONS OF n-HEPTYL ALCOHOL

Acid	*M*	Absorbance at 420 $m\mu$	Absorbance at 475 $m\mu$
HCl	0·05	0·105	0·070
HCl	0·1	0·130	0·098
HCl	0·2	0·095	
HCl	0·6	0·065	
H_3PO_4	0·05	0·050	
H_3PO_4	0·1	0·110	0·070
H_3PO_4	0·2	0·105	0·072
H_3PO_4	0·7	0·045	
$ClCH_2COOH$	0·05	0·095	
$ClCH_2COOH$	0·1	0·105	0·070
$ClCH_2COOH$	0·2	0·090	0·060
$ClCH_2COOH$	0·7	0·050	

and mechanical shaking was therefore substituted. Experiments were repeated with various shaking times, and it was found that the amount of vanadium reacting with di-iodo-oxine and extracted into the organic layer depends on the shaking time, *i.e.*, for the same shaking time the same amount of vanadium complex is always extracted. It was established that 15 μg of vanadium/ml of reagent solution can be extracted within 1 hr from 500-ml portions (Table II). This is also the concentration limit for the reagent solution. When more vanadium is present, smaller volumes of the aqueous solutions should be taken (50–100 ml) and the extraction time can be reduced to 15–20 min.

TABLE II.—INFLUENCE OF EXTRACTION TIME ON THE AMOUNT OF VANADIUM EXTRACTED

Vanadium in aqueous solution μg	Vanadium extracted into 5 ml of reagent solution μg					
	15	30	45	60	90	120 *min*
2·5	2·5	2·5				
5·0	5·0	5·0				
15	10	15	15			
25	10	25	25			
50	10	25	50	50		
75	10	25	50	75	75	
100	10	25	50	75	75	75

Masking of interfering cations

The interference of several cations in the determination of vanadium was studied. It was found that at the above-mentioned acid concentration Ca^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Al^{3+}, Cd^{2+}, Fe^{2+}, Pb^{2+}, UO_2^{2+}, ZrO_2^{2+} and Cu^{2+} do not interfere, when present in concentrations a hundred times that of the vanadium. Pronounced interference occurred from tervalent iron. Iron reacts with di-iodo-oxine in strongly acid solutions to form a green water-insoluble complex that is easily extracted by the same organic solvents as vanadium. The intensely green solutions absorb at the same wavelengths as vanadium. Iron is generally present in soil or plant tissue extracts in amounts hundreds of times those of vanadium, and so this source of interference has to be removed. Experiments to separate iron on ion-exchange columns proved unsatisfactory, as difficulties arose in elution of vanadium from the column. Attempts to complex iron with fluoride were also unsuccessful. The best results were obtained when iron was masked by phosphoric acid only: substitution of phosphoric acid for part of the hydrochloric acid used for establishing the acid concentration was found to have no advantage, so that in the final procedure phosphoric acid only was added. An excess of 3 ml of 4*M* phosphoric acid over the amount required for the optimum concentration of the vanadium solution is needed for the masking of 2–3 mg of iron.

Favourable comparison may be made with other methods proposed for the photometric determination of vanadium, *viz.* that with 8-hydroxyquinoline, described by Talvitie,[3] and that given in the critical survey of methods by Bock and Gorbach,[8] in both of which iron has to be separated initially. The molar absorptivity for 8-hydroxyquinoline computed from the Beer-Lambert curve of Bock and Gorbach[8] is 3200 at

485·5 mμ. The procedure described by Talvitie is very tedious, necessitating several extractions and purification of the chloroform.

The 5,7-di-iodo-8-hydroxyquinoline method has the double advantage of not requiring initial separation of iron, and of one single extraction being sufficient for good results. Taken together with the relatively high molar absorptivity (6000 at 420 mμ), these factors make it possible to determine vanadium in samples containing only 2·5 μg of it.

Acknowledgement—This work was carried out under Grant No. FG-Is-158 of the U.S. Department of Agriculture, for which the authors are duly grateful.

Zusammenfassung—Es wurde eine genaue spektrophotometrische Methode zur Bestimmung von 2,5–25 μg Vanadium in Volumina bis 500 ml Wasser entwickelt. Die Methode beruht auf der Anreicherung (100- bis 1000-fach) und Komplexbildung von Vanadium(V) mit Dijodoxin in einer mit Wasser nicht mischbaren Phase. Die Störung durch Eisen wird durch Maskierung mit Phosphorsäure beseitigt. Für Lösungen mit 5 μg Vanadium wurde eine Stantardabweichung von $\pm$0,04 μg ermittelt.

Résumé—On a élaboré une méthode spectrophotométrique précise de dosage de 2,5–25 μg de vanadium dans des volumes d'eau allant jusqu'à 500 ml. La méthode est basée sur la concentration (100–1000 fois) et la complexation simultanées du vanadium(V) par la diiodo-oxine dans une phase non miscible à l'eau. On élimine l'interférence du fer par dissimulation à l'acide phosphorique. L'écart type estimé est de $\pm$0,04 μg pour des solutions contenant 5 μg de vanadium.

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INVESTIGATION OF BIS(CARBOXYMETHYL)DITHIOCARBAMATE COMPLEXES BY THE EXTRACTION METHOD

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Summary—The extraction of copper, lead, cadmium, nickel and zinc dithizonates was investigated in the presence of ammonium bis(carboxymethyl)dithiocarbamate. For all metals studied, except zinc, masking of extraction was observed, depending on the amount of the dithiocarbamate in the aqueous phase. From the shift of the $pH_{1/2}$ values for dithizonate extraction, the stability constants β_2 for the metal complexes with bis(carboxymethyl)dithiocarbamate were calculated. The logarithms of the constants are 21·46, 15·45, 11·24 and 7·93 for the copper, lead, cadmium and nickel complexes respectively.

IN the course of our studies on the analytical application of dithiocarbamate complexes[1–4] we investigated the equilibria in solutions of these compounds and determined the constants which characterize these equilibria.[2,5,6]

The characteristics of a chemical compound which is used as a reagent for metal ions are defined by metal-binding functional groups and by analytical active groups which modify the properties of the metal complexes formed. The former group in the case of dithiocarbamate reagents consists of two donor sulphur atoms, but the latter may have either hydrophobic character, as in diethyldithiocarbamate, or may contain hydrophilic groups (*e.g.*, the carboxylic group present in the bis(carboxymethyl)dithiocarbamate molecule).[7] The presence of one[8,9] or two carboxymethyl groups significantly changes the properties of metal–dithiocarbamate complexes, making them readily soluble in water, but insoluble in the organic solvents commonly used in extraction. Taking these facts into account we tried to apply bis(carboxymethyl)dithiocarbamate as a selective masking reagent in dithizonate extractions and found that copper, lead, cadmium and nickel ions may be masked and do not interfere in the extraction of zinc dithizonate. In this paper we describe the determination of the stability constants of some metal–bis(carboxymethyl)dithiocarbamate complexes, from measurements based on the competition of two ligands for the same metal in the water–carbon tetrachloride system.

EXPERIMENTAL

Reagents

Solutions of Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+} and Ni^{2+}, all 0·1*M*, were prepared from the nitrates or from the metals dissolved in nitric acid, and were standardized complexometrically.

Dithizone (HDz), 0·01% in carbon tetrachloride, was prepared from the purified reagent.[10] Its concentration was determined by argentometric extractive titration and checked spectrophotometrically.

Ammonium bis(carboxymethyl)-dithiocarbamate (DTC), 0·1*M* in dilute sodium hydroxide was prepared and standardized by the method previously described.[11]

Other reagents were prepared by the usual procedures and were purified by dithizone extraction.

Apparatus

Absorptiometric measurements were made with a Pulfrich photometer with photoelectric attachment (Carl Zeiss). Measurements of pH were made with a Radiometer pHM-22 instrument, with glass and calomel electrodes.

Procedure

For each metal ion two series of measurements were performed. In the first the dithizonates were extracted from non-complexing solutions in order to determine the molar absorptivities of the dithizonates and the $pH_{1/2}$ of the non-masked extraction under the given experimental conditions. In the second series, in the presence of different concentrations of bis(carboxymethyl)dithiocarbamate, the degree of extraction was determined and from the results the $pH_{1/2}$ for extraction from masked solutions was calculated.

Extraction was performed from 15 ml of aqueous solution that was 10^{-4}–$10^{-5}M$ in metal ion, $10^{-2}M$ in buffer solution (where necessary) and $0{\cdot}1M$ in potassium nitrate. In the second series the concentration of masking reagent ranged from 10^{-2} to $10^{-4}M$. The organic phase consisted of 15 ml of dithizone solution in carbon tetrachloride. Dithizone was used in approximately 10-fold excess. The equilibration time for extraction was estimated for each ion separately and ranged from 5 to 15 min. The excess of unreacted dithizone was removed by stripping twice with dilute ammonia solution of such a concentration that it did not affect the absorbance of the dithizonates even after a prolonged stripping period. Finally, the concentration of metal dithizonate in the carbon tetrachloride was determined absorptiometrically. The pH value of the aqueous layer was measured. For each masking concentration and pH the measurements were performed for several metal ion concentrations, and the absorbance of the blank was subtracted. These conditions were chosen because they most closely resemble those used in analytical separation procedures. In all experiments the temperature was maintained at $20 \pm 1°$.

RESULTS AND DISCUSSION

In the system DTC–metal ion–HDz several equilibria must be considered when quantitative results are needed. In the pH range of non-masked extraction the ions Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+} and Ni^{2+} do not form hydroxo-complexes which might disturb the main reaction. When buffers were used, their concentration was less than $10^{-2}M$. The buffering substances were selected so that the logarithm of the stability constant of their complex with a given metal was not greater than 0·1. Under such conditions no interfering side-reactions need to be considered, and the total concentration of the metal in the aqueous phase is the concentration of the hydrated metal ion. The salt concentration was kept constant except for the non-masked extraction of copper dithizonate in strongly acid medium. Nevertheless the change of activity coefficients should not affect the value of the logarithm of the stability constant by more than 0·2, which is within the limits of experimental error.

The masked extractions were performed in more alkaline solutions. However, in the presence of large enough concentrations of strong masking agents the concentration of hydroxo-complexes may be neglected in comparison with that of the complexed metal ion.

Dithizone, present initially in the organic solvent, has weakly acidic properties. Its dissociation constant[12] K_{HDz} is $10^{-4{\cdot}5}$, and its distribution coefficient P_{HDz} $10^{4{\cdot}0}$ in the water–carbon tetrachloride system. When dithizone is shaken with alkaline solutions, pH > 7·5, its dissociation causes a decrease of the equilibrium dithizone concentration in the carbon tetrachloride phase, according to the equation:

$$\alpha_{HDz} = \frac{[HDz]_o}{[HDz] + [Dz^-]} = \frac{P_{HDz}}{1 + K_{HDz}/[H^+]} \qquad (1)$$

where the subscript *o* denotes the species in the organic phase. From this it follows that for dithizone $pH_{1/2}$ is 8·50. The decrease of dithizone concentration in the organic phase has a significant influence on the shape of the extraction–pH curves, which have in all cases a smaller slope than expected for a reaction involving two protons.

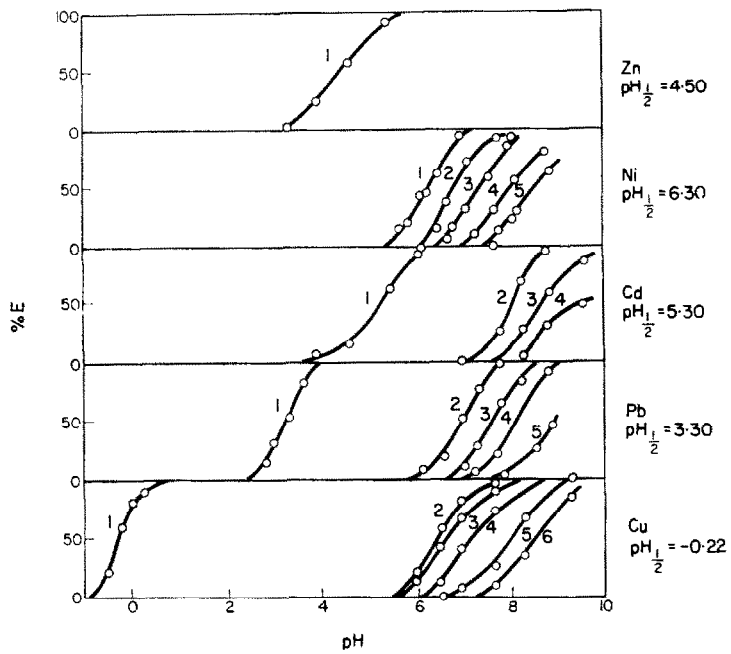

FIG. 1.—Extraction *vs.* pH curves for metal dithizonate extraction. For all metals curve (1) is for non-masked extraction.

Ni; [DTC] *2*—2×10^{-4} *M*; *3*—10^{-3} *M*; *4*—2×10^{-3} *M*; *5*—10^{-2} *M*

Cd; [DTC] *2*—10^{-3} *M*; *3*—2×10^{-3} *M*; *4*—10^{-2} *M*

Pb; [DTC] *2*—10^{-4} *M*; *3*—$3{\cdot}3 \times 10^{-4}$ *M*; *4*—10^{-3} *M*; *5*—$3{\cdot}3 \times 10^{-3}$ *M*

Cu; [DTC] *2*—6×10^{-5} *M*; *3*—2×10^{-4} *M*; *4*—6×10^{-4} *M*; *5*—2×10^{-3} *M*; *6*—6×10^{-3} *M*

In the case of a masked extraction at pH $\geqslant$ 6, the total concentration of the masking reagent may be assumed equal to the concentration of the free ligand because the estimated value of the dissociation constant is not smaller than $10^{-4{\cdot}5}$. The complete dissociation of the dithiocarbamic acid in this pH range implies a sufficient stability of the ligand, for which the half-life at pH 6 is 2 hr.[7] Further, because a large excess of the masking ligand was used, the amount bound to metal ions may be neglected. Although the formation of mixed complexes containing both competing ligands when these are of such different character is highly improbable, this possibility was checked spectrophotometrically by comparison of the spectra with those of corresponding complexes obtained in the absence of a second ligand.

Absorptiometric determinations of the amount of the dithizonate formed served as a basis for plotting the extraction–pH curves (Fig. 1). From these curves the

$pH_{1/2}$ values for non-masked and masked extraction at different bis(carboxymethyl)-dithiocarbamate concentrations were evaluated.[13,14,15] Accepting the aforementioned simplifying assumptions for the non-masked extraction

$$M^{2+} + 2(HDz)_o = (MDz_2)_o + 2H^+, \tag{2}$$

the distribution ratio is

$$D = K\frac{[HDz]_o^2}{[H]} \tag{3}$$

where K represents the extraction constant for the metal dithizonate. At $pH_{1/2}$ the distribution ratio is unity, and thus:

$$2pH_{1/2} = -\log K - 2\log [HDz]_o. \tag{4}$$

In the conditions of the masked reaction, *i.e.*, in the presence of an excess of bis-(carboxymethyl)dithiocarbamate, hydrated metal ions and complexes formed stepwise occur in the solution. The contribution of each particular species depends on the values of the stability constants β_i for the various complexes and on the concentration of free ligand (DTC), and may be described by the complexation function F:

$$F = \sum_{i=0}^{N} \beta_i [DTC]^i$$

where

$$\beta_0 = 1. \tag{5}$$

Thus, for the masked extraction the distribution ratio D^* is

$$D^* = K\frac{[HDz]_o^{*2}}{[H]^{*2}F} \tag{6}$$

where K has the same value as in equation (3), and

$$-\log K = 2\log [HDz]_o^* + 2pH_{1/2}^* - \log F \tag{7}$$

where symbols with an asterisk refer to the masked extraction. From equations (4) and (7) the value of $\log F$ may be calculated:

$$\log F = 2(pH_{1/2}^* - pH_{1/2}) + 2\log\frac{[HDz]_o^*}{[HDz]_o} \tag{8}$$

The equilibrium concentration of dithizone was calculated from its total amount and the amount bound in the metal dithizonate, taking into account the distribution ratio of dithizone at various pH values [equation (1)].

The corresponding experimental data are given in Table I. The logarithm of the complexation function calculated on this basis was plotted *vs.* the logarithm of the ligand concentration (Fig. 2). In the concentration range studied, the linear relationship at a slope of 2 indicates clearly that the dominating complex has the metal to ligand ratio 1:2. The calculated overall stability constants β_2 are also given in Table I for individual measurements. These data indicate clearly the composition of the

TABLE I.—DETERMINATION OF STABILITY CONSTANTS OF METAL–BIS(CARBOXYMETHYL)DITHIOCARBAMATE COMPLEXES IN 0·1*M* KNO_3 AT 20°C

Metal ion	$pH_{1/2}$	log [DTC]	log F	log β_2	Mean log β_2
Cu^{2+}	−0·22	—	—	—	
	6·45	−4·22	13·34	21·78	
	6·75	−3·70	13·94	21·34	
	7·20	−3·22	14·84	21·28	
	8·05	−2·70	16·26	21·66	
	8·60	−2·22	16·92	21·26	21·46
Pb^{2+}	3·30	—	—	—	
	7·01	−4·00	7·42	15·42	
	7·70	−3·48	8·68	15·64	
	8·36	−3·00	9·62	15·62	
	9·00	−2·48	10·16	15·12	15·45
Cd^{2+}	5·36	—	—	—	
	8·12	−3·00	5·26	11·26	
	8·20	−2·88	5·28	11·04	
	8·70	−2·70	5·86	11·26	
	9·00	−2·00	7·40	11·40	11·24
Ni^{2+}	6·30	—	—	—	
	6·80	−3·48	1·00	7·96	
	7·42	−3·00	1·92	7·92	7·93
	8·00	−2·48	3·28	8·04	
	8·55	−2·00	3·78	7·78	
Zn^{2+}	4·50	—	—	—	<4·5
	4·50	−2·00			

complexes formed. An additional proof should be obtainable from the slope of the log D *vs.* log [DTC] curve. However, in our case this method failed because the dithizone concentration changed in individual measurements owing to its dissociation, and because the excess of dithizone was not greater than ten times the concentration of the metal ion. In these experiments the extraction conditions were chosen to be as similar as possible to those used in analytical separations and therefore a larger excess was avoided. Nevertheless, considering the fact that for different concentrations of excess of dithizone the equilibrium may be established in a slightly different manner, the values of $pH_{1/2}$ seem to be the most accurate and the most reproducible measure of this equilibrium.

The values of stability of bis(carboxymethyl)dithiocarbamate complexes may be compared with the values pK_{sp} (where K_{sp} is the solubility product) of the corresponding diethyldithiocarbamate complexes, which are 29·55, 21·68, 22·03, 23·07 and 16·93 for copper, lead, cadmium, nickel and zinc respectively.[2]

It is interesting that in the case of the bis(carboxymethyl)dithiocarbamate complexes the sequence of stability of cadmium, nickel and lead complexes is different from the sequence of the solubility products of the diethyldithiocarbamates of these metals. The high stability of the lead complex may be at least partially attributed to its greater tendency to form chelates with ligand groups containing oxygen donor atoms, as for example with the carboxyl groups in bis(carboxymethyl)dithiocarbamate. This additional bonding may be responsible for the stability of the lead complex. Another factor which probably decreases the solubility of nickel diethyldithiocarbamate might be the possibility of the precipitate aging in a manner similar to that of nickel sulphide precipitates.

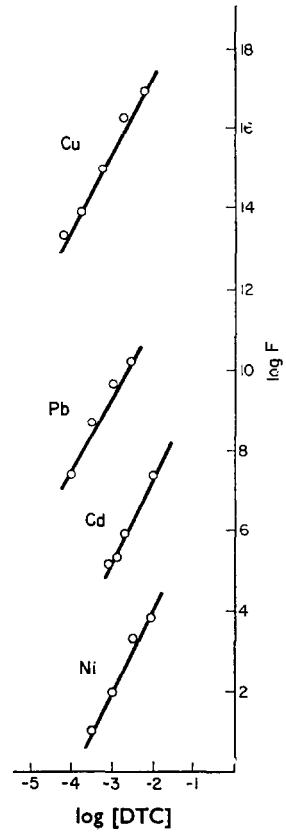

FIG. 2.—The complexation function for metal–bis(carboxymethyl)dithiocarbamate complexes.

The value of the stability constant of the copper complex may also be compared with the value of the constant determined by Janssen[16] for the 3-carboxy-cyclopentamethylenedithiocarbamate–copper complex. The logarithm of this constant is 22·4, slightly greater than in our case, which is in agreement with the statement that the introduction of the additional carboxyl group into the ligand molecule may decrease its complexing ability.

Acknowledgement—The authors are indebted to Prof. Dr. W. Kemula, Head of the Department of Inorganic Chemistry, University of Warsaw, for helpful and stimulating comments and discussions.

Zusammenfassung—Die Extraktion der Dithizonate von Kupfer, Blei, Cadmium, Nickel und Zink wurde in Gegenwart von Ammoniumbis-(carboxymethyl)dithiocarbamat untersucht. Bei allen untersuchten Metallen außer Zink wurde Maskierung der Extraktion beobachtet, je nachder Menge Dithiocarbamat in der wäßrigen Phase. Aus der Verschiebung der $pH_{1/2}$-Werte der Dithizonatextraktion wurden die Stabilitätskonstanten β_2 der Metallkomplexe mit Bis(carboxymethyl) dithiocarbamat berechnet. Die Logarithmen der Konstanten sind 21,46; 15,45; 11,24 und 7,93 für die Komplexe von Kupfer, Blei, Cadmium und Nickel.

Résumé—On a étudié l'extraction des dithizonates de cuivre, plomb, cadmium, nickel et zinc, en présence de bis(carboxyméthyl)dithiocarbamate d'ammonium. Pour tous les métaux étudiés, à l'exception du zinc, on a observé un blocage de l'extraction, dépendant de la quantité de dithiocarbamate dans la phase aqueuse. A partir du changement des valeurs du $pH_{1/2}$ pour l'extraction des dithizonates, on a calculé les constantes de stabilité β_2 pour les complexes métalliques avec le bis (carboxyméthyl)dithiocarbamate. Les logarithmes des constantes sont 21,46; 15,45; 11,24 et 7,93 pour les complexes de cuivre, plomb, cadmium et nickel respectivement.

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SHORT COMMUNICATIONS

The separation of arsenic(V) and (III) by thin-layer chromatography

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ANION-exchange,[1] paper electrophoresis[2] and paper chromatography,[3] as well as the classical precipitation method have been utilized for the separation of arsenic(V) and (III). These methods are effective, but take considerable time to achieve the complete separation. Thin-layer chromatography (TLC) should be very suitable on account of its simplicity, speed, efficiency of separation and sensitivity of detection. The separation of arsenic(V) and (III) by TLC in a butanol–benzene–1*M* nitric acid–1*M* hydrochloric acid (50:46:2·6:1·4) solvent system has been reported briefly. Complexity of the system and possible oxidation of arsenic(III) to (V) would hamper the utility of the method, and so would the rather long development time involved (45 min).

The present investigation was undertaken to provide simpler and more rapid TLC systems for the separation of arsenic(V) and (III), and suggests the use of an acetone–phosphoric acid mixture (50:1) as a satisfactory developing agent.

EXPERIMENTAL

Stock solutions of arsenic(III) and (V), (both 10 μg/μl) were prepared by dissolving appropriate amounts of arsenic(III) oxide and disodium hydrogen arsenate heptahydrate, in dilute sodium hydroxide solution and water respectively, and diluting with water to a definite volume. A test solution was made by mixing an equal volume of both solutions. The solvent systems used to develop the chromatograms were

A acetone–phosphoric acid (50:1)
B acetone–phosphoric acid (4:1)
C ethanol–phosphoric acid (50:1)
D butanol–phosphoric acid (50:1).

The concentration of phosphoric acid was varied over the range from 1 to 15*M* in each system except for *B*, in which the phosphoric acid was varied from 1 to 6*M* in concentration.

A commercial silica gel containing 5% of calcium sulphate was slurried with water and spread 250 μ thick on 2·5 × 20 cm^2 plates from an applicator. The plates were then air-dried overnight at room temperature. The thin-layers were spotted 25 mm from one end with one dab (about 1–2 μl) of the test solution from a glass capillary, and dried in air for 20 min. The plates were then placed in the developing chamber containing the developing solvent and allowed to stand for 20 min to permit equilibration of the atmosphere inside. Development was conducted by the ascending technique until the solvent front had risen 12 cm. Subsequently the plates were dried in air and the spots visualized by spraying first with saturated tin(II) chloride solution and then with 5% sodium thiosulphate solution. Both arsenic(III) and (V) were detected as yellow spots.

RESULTS AND DISCUSSION

In Fig. 1 the behaviour of arsenic(V) and (III) in the solvent systems *A* to *D* is illustrated. The components of the solvent move at different rates so that the organic phase advances rapidly and the aqueous phosphoric acid front moves slowly behind it. Two fronts are distinguishable in each solvent system. It is of interest to note that the phosphoric acid front always carries the arsenic(V) with it. This may be due to the formation of undissociated arsenic acid molecules, which is favoured in the presence of the much stronger phosphoric acid. In contrast, the arsenic(III) ion will react with phosphoric acid to yield $AsPO_4$,[5] which is only slightly soluble in organic solvents such as acetone and ethanol, thus remaining at or near the start of the chromatogram. As can be seen in Fig. 1b, increasing the ratio of phosphoric acid to acetone results in broadening of the spots of both arsenic(V) and (III). In addition the values of arsenic(V) decrease with increasing concentration of phosphoric acid, provided that the acetone-phosphoric acid ratio is kept constant at 4:1.

The behaviour of arsenic(V) and (III) in mixtures of ethanol and phosphoric acid is almost the same as in the acetone–phosphoric acid (50:1) solvent system (Fig. 1c). However, part of the

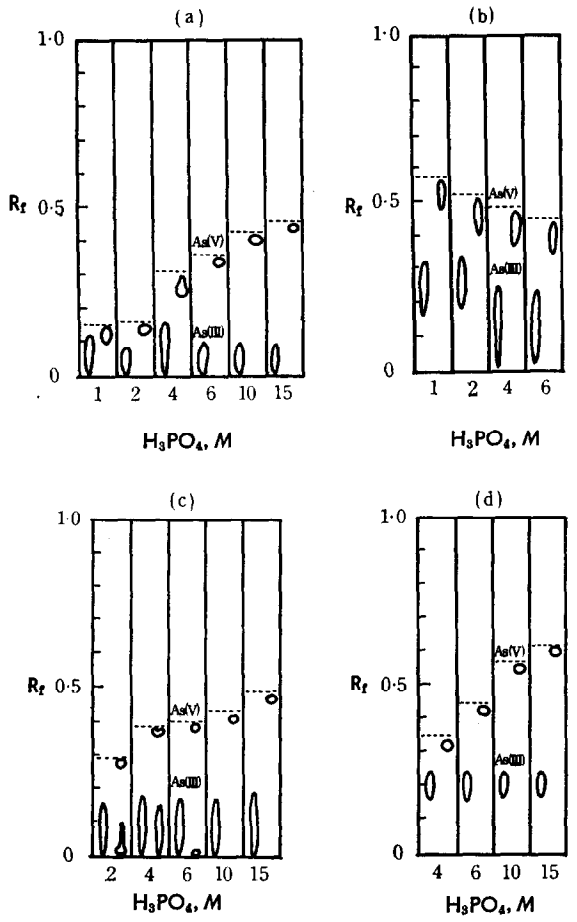

FIG. 1.—The behaviour of As(III) and As(V) in different solvent systems.
(*a*) Acetone–H_3PO_4 (50:1)
(*b*) Acetone–H_3PO_4 (4:1)
(*c*) Ethanol–H_3PO_4 (50:1)
(*d*) Butanol–H_3PO_4 (50:1)
– – – Phosphoric acid front

arsenic(V) is retained at the original spot, possibly because of partial reduction to arsenic(III), if the concentration of phosphoric acid is less than 6*M*.

Just as in the acetone–phosphoric acid (50:1) solvent, R_f values for arsenic(V) increase regularly with increasing concentration of phosphoric acid in the butanol–phosphoric acid system. R_f values for arsenic(III) remain constant at approximately 0·2 regardless of the phosphoric acid concentration. Greater solubility of $AsPO_4$ in butanol could account for the rather high R_f value for arsenic(III) in this system.

Other solvent systems were also tested, *e.g.*, isopropanol–phosphoric acid (50:1) with 6–15*M* acid, and acetone–benzene–15*M* phosphoric acid (20:20:1), but all without success. Based on these observations, phosphoric acid coupled with acetone or butanol should provide a satisfactory solvent for the effective separation of arsenic(V) and (III). The more concentrated the phosphoric acid, the more effective is the separation, provided the volume ratio of organic solvent to phosphoric acid is kept at 50:1. However, the time required to make the solvent front rise 12 cm, which is sufficient for good separation, depends markedly on the organic solvent used; *e.g.*, ~20 min for acetone–phosphoric acid (50:1), ~25 min for acetone–phosphoric acid (4:1), ~60 min for ethanol–phosphoric acid (50:1) and ~120 min for butanol–phosphoric acid (50:1). The solvent system acetone–15*M* phosphoric acid (50:1) may be recommended as suitable for rapid separation. Results for the practical separation of arsenic(V) and (III) in four solvent systems are illustrated in Fig. 2.

Acknowledgement—The author is indebted to Professor Rokuro Kuroda, University of Chiba for his helpful suggestions throughout the work.

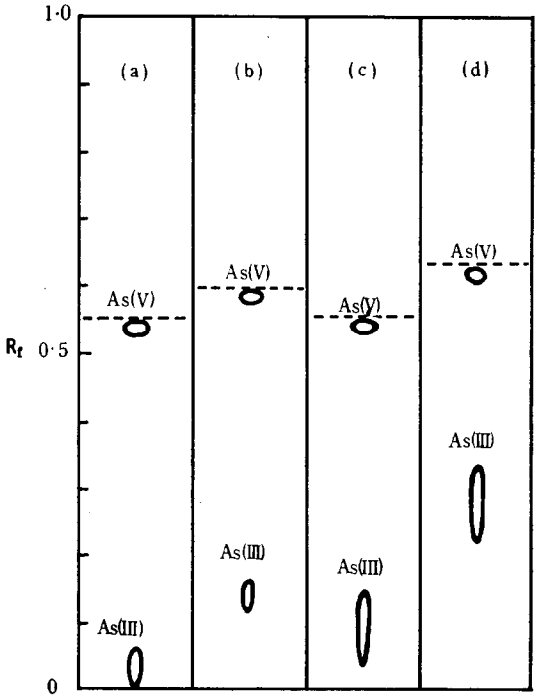

FIG. 2.—The separation of As(III) and As(V).
(*a*) Acetone–15*M* H_3PO_4 (50:1)
(*b*) Butanol–15*M* H_3PO_4 (50:1)
(*c*) Ethanol–15*M* H_3PO_4 (50:1)
(*d*) Acetone–1*M* HP_3O_4 (4:1)
– – – Phosphoric acidfront

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Summary—The separation of arsenic(III) and (V) can be effected by ascending chromatography on a silica gel thin-layer containing 5% of calcium sulphate. An acetone-15*M* phosphoric acid (50:1) solvent system gives the most satisfactory separation. The method is rapid, taking only 20 min to complete the separation.

Zusammenfassung—Arsenik(III) und -(V) können durch aufsteigende Chromatographie an einer 5% Calciumsulfat enthaltenden Kieselgel-Dünnschicht getrennt werden. Am besten wirkt ein Lösungsmittelsystem aus Aceton und 15*M* Phosphorsäure (50:1). Die Methode geht schnell; die Trennung ist schon nach 20 min beendet.

Résumé—On peut effectuer la séparation des arsenic(III) et (V) par chromatographie ascendante sur une couche mince de gel de silice contenant 5% de sulfate de calcium. Un système solvant acétone–acide phosphorique 15*M* (50:1) donne la séparation la plus satisfaisante. La méthode est rapide, ne nécessitant que 20 mn pour réaliser la séparation.

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Extractive photometric determination of lanthanides and yttrium with Chlorophosphonazo DAL

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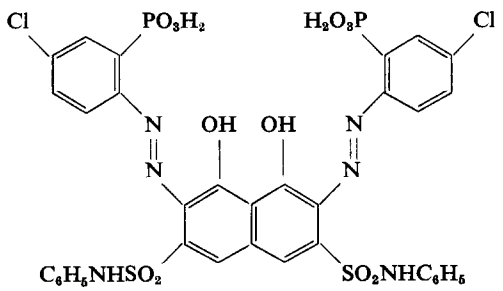
THE formation of dianilides of 3,6-bisphenylazo derivatives of chromotropic acid is an advantageous way of transforming known photometric reagents, such as Arsenazo III, Chlorophosphonazo III, Sulphonazo III, *etc.*, into extractable substances.[1] Thus Chlorophosphonazo DAL, *i.e.*, the dianilide of 3,6-bis(*p*-chloro-*o*-phosphonophenylazo)-chromotropic acid (I) is a convenient extractive photo-



(I)

metric reagent for uranium (VI), uranium(IV), thorium, zirconium, hafnium, lanthanides, yttrium calcium, strontium and barium.[2] The reaction with lanthanides and yttrium is very sensitive and can be used advantageously for determination of trace amounts of these elements. It is necessary, however, to remove uranium(VI) first.

Preparation of the reagent solution

Dissolve 91 mg of Chlorophosphonazo DAL in about 250 ml of 0·1*M* sodium hydroxide. Add 1000 ml of n-butanol and about 250 ml of 0·5*M* hydrochloric acid. Shake for 2–3 min and then separate from the aqueous layer. Wash the butanol phase 3–4 times with 250 ml of water until the pH of the aqueous phase is 5–6. The concentration of reagent does not need to be accurately known, so loss of butanol in the washing procedure is unimportant. The reagent solution is stable for several months.

Procedure

Add 5 ml of a 0·01*M* solution of the diammonium salt of DCTA* for every 10 ml of sample solution. Adjust the acidity to 1·8–2·2 with 0·1*M* sodium hydroxide and 0·1*M* hydrochloric acid (use a pH meter or make the solution just acid to Methyl Red) and dilute to a convenient standard volume. Place a 10-ml aliquot of sample solution, containing 0·005–0·1 μmole of lanthanides and of yttrium, in a separatory funnel. Add 0·3 ml of 0·1*M* hydrochloric acid, 10·0 ml of the reagent solution and shake vigorously for 3–5 min. After clarification of the butanol phase, place an appropriate volume of it in a 1-cm cell and measure its absorbance at 670 mμ against a reagent blank.

Results and remarks

Typical results of lanthanide and yttrium determinations are summarized in Table I. At the recommended pH the reagent solution has maximum absorbance at 540 mμ. The absorption maxima of the lanthanide-Chlorophosphonazo DAL complexes in butanol all occur at 670 mμ and at this wavelength the net molar absorptivities are: yttrium 64500, lanthanum 53500, cerium(III) 22500, praseodymium(III) 20500, neodymium 17500, samarium(III) 29500, europium(III) 19500, gadolinium 57500, terbium 50000, dysprosium 52500, holmium 80000, erbium 64000, thulium 40000, ytterbium(III) 42000, and lutetium 38000 (all in cm^2 $mmole^{-1}$). In a 10-ml aliquot of sample solution, 20–30 μmole amounts of zirconium, hafnium, iron(III), magnesium, calcium, strontium and barium, 5 μmole amounts of fluoride, phosphate, Tiron, and chromotropic acid, or 1 mmole amounts of chloride, nitrate, perchlorate and sulphate do not interfere. Thorium interferes if 0·05 μmole is present, and so does 0·02 μmole of uranium(VI).

* Prepared by dissolving 3·46 g of DCTA in 250 ml of 0·08*M* aqueous ammonia and diluting to 1 l. with water. DCTA is 1,2-diaminacyclohexanetetra-acetic acid.

TABLE I

Taken, μg			Metals added, mmole	Found, μg		
0·69 La			—	0·65 La		
1·38			—	1·40		
13·89			—	13·96		
0·82 Ho			0·03 Zr	0·74 Ho		
1·65			0·03	1·67		
16·25			0·03	16·66		
1·50 Sm			0·02 Fe(III)	1·47 Sm		
15·03			0·02	15·03		
1·75 Lu			0·02 Hf	1·68 Lu		
17·50			0·02	17·43		
0·78 Gd			4·0 U(VI)*	0·85 Gd		
1·57			4·0	1·55		
15·72			4·0	15·84		
0·44 Y			2·0 Cu(II)*	0·45 Y		
0·88			2·0	0·84		
1·62 Dy			3·0 Cd	1·65 Dy		
16·25			3·0	16·44		
0·69 La			4·0 Zn*	0·73 La		
1·38			4·0	1·40		
0·69			0·003 Th†	0·74		
1·38			0·003	1·43		
0·78 Gd	6·96 Th	2·40 Ca	3·0 U(VI)‡	0·86 Gd	6·91 Th	2·52 Ca
1·57	13·92	4·80	3·0	1·62	14·45	5·43
15·72	20·88	7·20	3·0	15·79	20·41	7·83
0·82 Ho	13·92 Th	4·80 Ca	3·0 Cd‡	0·90 Ho	14·05 Th	4·85 Ca
1·65	20·88	7·20	3·0	1·68	20·41	7·36
13·89 La	5·31 Th		¶	14·23 La	5·22 Th	
9·14	4·85		¶	9·41	4·76	

* Preliminary extraction with tri-iso-octylamine.

† Preliminary extraction of thorium with 8-hydroxyquinoline.

‡ Systematic stepwise extraction with tri-iso-octylamine, Arsenazo DAL and Chlorophosphonazo DAL, and calcium determination with Chlorophosphonazo III.

¶ Analysis of monazite sands by application of stepwise extraction with tri-iso-octylamine, Arsenazo DAL and Chlorophosphonazo DAL. The results obtained for thorium and lanthanides are compared with the Arsenazo method for thorium[6] and the gravimetric determination of the sum of the lanthanides.[5]

Larger amounts, 1–4 mmole, of uranium(VI), vanadium(V), niobium(V), cobalt(II), copper(II), lead, iron(III), chromium(VI), molybdenum(VI), zinc and cadmium, can be removed by extraction with three 20-ml portions of 20% w/v solution of tri-iso-octylamine in xylene from 7*M* hydrochloric acid. The excess of acid is evaporated before the determination of lanthanides and yttrium.

Thorium (1–3 μmole) is removed by extraction with three 10-ml portions of 1% w/v solution of 8-hydroxyquinoline in chloroform at pH 3·0–3·5. The aqueous phase may be used directly for the lanthanide and yttrium determination.

A systematic stepwise procedure, consisting of extraction with tri-iso-octylamine, followed by an extractive thorium determination by means of Arsenazo DAL,[3] determination of lanthanides and yttrium as described here, and finally calcium determination with Chlorophosphonazo III,[4] is advantageous for the determination of trace amounts of thorium, yttrium, lanthanides, and calcium in uranium, cobalt, copper, iron, zinc, cadmium, *etc.*, and for analysis of some mineral ores. Sintering

with sodium peroxide has been used for decomposition of mineral ores.[5] After the extraction of yttrium and lanthanides, the solution must be evaporated to dryness and the residue ignited at 500–600° before the calcium determination.

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Summary—Chlorophosphonazo DAL, *i.e.*, the dianilide of 3,6-bis(*p*-chloro-*o*-phosphonophenylazo) chromotropic acid, is proposed as an extractive photometric reagent for determination of trace amounts of yttrium and lanthanides in uranium, cobalt, copper, iron, zinc, cadmium and mineral ores.

Zusammenfassung—Chlorphosphonazo DAL, d.h. Dianilid der 3,6-Bis(*p*-chlor-*o*-phosphonophenylazo)chromotropsäure, wird als extraktionsphotometrisches Reagens zur Bestimmung von Spurenmengen des Yttriums und der Lanthanide in Uran, Kobalt, Kupfer, Eisen, Zink, Cadmium und Erzen vorgeschlagen.

Résumé—On a proposé le Chlorophosphonazo DAL, c'est-à-dire le dianilide de l'acide 3,6-bis (*p*-chloro-*o*-phosphonophénylazo) chromotropique, comme réactif photométrique par extraction pour le dosage de traces d'yttrium et de lanthanides dans l'uranium, le cobalt, le cuivre, le fer, le zinc, le cadmium et les minerals minéraux.

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The precipitation of bismuth basic acetate from homogeneous solution

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BISMUTH may be precipitated as its basic nitrate by urea hydrolysis in dilute nitric acid solution. Precipitation is complete at about pH 3, but in the absence of a buffer the pH rises at an uncontrollable rate at the end of precipitation to above pH 6. Formate ions exert a satisfactory buffer action, and the precipitation of bismuth basic formate by urea hydrolysis has been described.[1] However, in the presence of a large excess of formic acid some reduction to bismuth occurs, and care is necessary in igniting the precipitate since the conversion into oxide is rapid and may cause losses. Since acetate ions have a similar buffer action to formate ions the precipitation of bismuth basic acetate from homogeneous solution was studied to determine whether the method offered any advantages.

EXPERIMENTAL

All reagents were of analytical grade. A stock solution was prepared containing 10 g of bismuth per l.

Procedure

The reaction solutions containing bismuth (5·0 g), urea (50 g) and various amounts of acetic acid in a total initial volume of 550 ml were gently boiled under reflux to minimize losses due to evaporation.

with sodium peroxide has been used for decomposition of mineral ores.[5] After the extraction of yttrium and lanthanides, the solution must be evaporated to dryness and the residue ignited at 500–600° before the calcium determination.

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EXPERIMENTAL

All reagents were of analytical grade. A stock solution was prepared containing 10 g of bismuth per l.

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The reaction solutions containing bismuth (5·0 g), urea (50 g) and various amounts of acetic acid in a total initial volume of 550 ml were gently boiled under reflux to minimize losses due to evaporation.

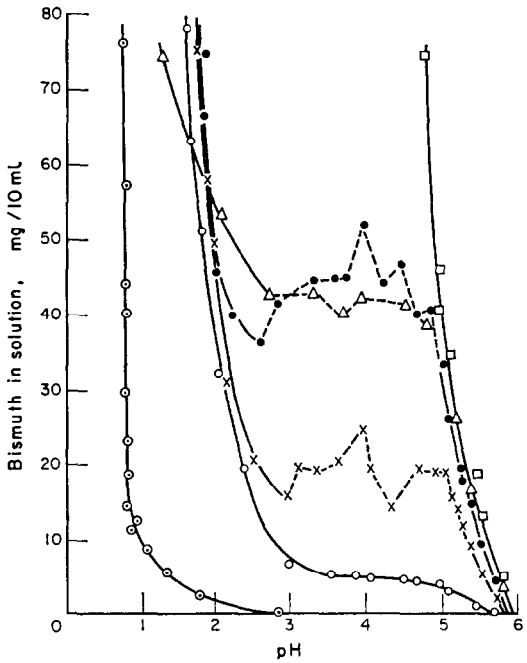

FIG. 1.—Precipitation of bismuth basic acetate.
Urea hydrolysis: ○—25 ml of acetic acid; ×—50 ml; ●—75 ml; ⊙—no acetic acid.
Addition of ammonia: △—hot solution; □—room temperature.

Samples were removed at intervals from the boiling solution, cooled to stop the hydrolysis reaction and filtered to remove precipitate particles. The pH values of the cooled samples were measured and the amount of bismuth remaining in solution was determined by titration with standard EDTA solution, Pyrocatechol Violet being used as indicator. A blank determination was carried out in the absence of acetic acid. The results are shown in Fig. 1.

For comparison purposes precipitation was also brought about by the direct addition of ammonia to reaction solutions containing bismuth (5·0 g) and acetic acid (75 ml) in an initial volume of 550 ml, both at room temperature and in boiling solution. The results are included in Fig. 1.

Determination of bismuth

Take a solution containing up to 250 mg of bismuth, add 2–4 ml of acetic acid (glacial) and 10 g of urea, dilute the solution to 300 ml and boil it. When precipitation begins add a few drops of Bromocresol Green solution and continue boiling until the indicator turns blue. Filter off the precipitate on a sintered porcelain crucible, wash it, and dry it at 120° before igniting it to bismuth oxide.

DISCUSSION

Ammonium acetate formed during the reaction provided an efficient buffer and the rate of increase of pH was easily controlled at all stages of precipitation. No reduction to metallic bismuth occurred.

Between pH 3 and 5 the results obtained in the presence of 50 ml and 75 ml of acetic acid followed a random pattern denoted in Fig. 1 by broken lines. Over this pH range the solubility of the precipitate varied widely with temperature being higher in cold solutions than in boiling solutions. When a hot solution at pH 3·5 containing some precipitate, 50 ml of acetic acid and *ca.* 2 mg of bismuth per ml was allowed to cool to room temperature, much of the precipitate in the reaction vessel redissolved and the bismuth content of the solution increased to 7 mg/ml. On re-heating of the solution, the precipitate was immediately reformed. In the experiments leading to the curves in Fig. 1 the samples removed from the boiling solutions contained precipitate particles. During cooling and filtering some of the precipitate redissolved, the amount passing into solution depending on the

amount initially present and the time taken to cool and filter. The results between pH 3 and 5 represent only approximately the amounts of bismuth in hot solution and for this reason are joined by broken lines. Above pH 5 the solubility of the precipitate was not markedly temperature dependent, and precipitation followed a smooth curve to completion.

Similar results were obtained when precipitation was brought about by the direct addition of ammonia, so the erratic behaviour was not due to the presence of urea. The solubility of the precipitate formed at pH 3·5 was tested in solutions containing the various ions present in the reaction solution at that pH. The precipitate was dissolved by acetate ions but was not affected by nitrate and ammonium ions or by urea.

The behaviour of the precipitate could be explained by the formation of acetate complexes of bismuth although it must be stressed that the existence of complexes has not been proved. Aluminium, for example, does not form a basic acetate until the solution is heated, owing to the existence of polynuclear aquo-complexes which are stable in cold solution. A similar behaviour on the part of bismuth may account for the fact that precipitation of basic acetate does not occur in cold solution till about pH 5·0, whereas in hot solution precipitation starts at about pH 2. A peculiarity of the bismuth system is the negative temperature dependence of the solubility in the pH range 3–5. This could be due to the formation of soluble acetate complexes that are unstable in hot solution, but in the absence of definite proof this must remain as a tentative explanation.

The precipitates formed by the homogeneous method were denser and more easily filtered off than those obtained by direct addition of ammonia. In the early stages of the reaction the precipitate adhered strongly to the walls of the vessel, but was more readily detached from the walls as the pH value of the solution rose above about pH 4. Microscopic examination of the precipitate showed it to consist largely of small discrete particles up to about pH 3. The precipitate obtained above pH 5 consisted of aggregates of small particles. The precipitate was readily ignited to bismuth oxide, but the conversion occurred more slowly than with bismuth basic formate and there was less danger of loss of precipitate during ignition.

When the method was applied to the determination of bismuth satisfactory recoveries were obtained (99·7–100·0%, mean value 99·9% for 5 determinations at the 250-mg level.) No difficulties were experienced in handling precipitates containing up to 0·5 g of bismuth. Attempts to separate bismuth from lead were unsuccessful owing to coprecipitation of lead. Although the use of acetate offers certain advantages over the use of formate in avoiding risk of reduction and facilitating ignition of the precipitate the method is not suitable for the determination of bismuth in the presence of lead.

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Summary—Precipitation from homogeneous solution by urea hydrolysis has been used to investigate the conditions affecting the precipitation of bismuth basic acetate. Evidence has been found that indicates that acetate complexes may be formed. The method has been tested for the determination of bismuth, but is not suitable if lead is present.

Zusammenfassung—Die Fällung aus homogener Lösung durch Hydrolyse von Harnstoff wurde benutzt, um die Bedingungen zu erforschen, die Einfluß auf die Fällung von basischem Wismutacetat haben. Es wurden Hinweise auf Bildung von Acetatokomplexen gefunden. Die Methode wurde zur Wismutbestimmung getestet, ist aber in Gegenwart von Blei ungeeignet.

Résumé—On a utilisé la précipitation en solution homogène par hydrolyse de l'urée pour étudier les conditions affectant la précipitation de l'acétate basique de bismuth. On a trouvé des faits indiquant que des complexes acétiques peuvent se former. On a essayé la méthode pour le dosage du bismuth, mais elle ne convient pas en présence de plomb.

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DETERMINATION OF TRACE AMOUNTS OF SULPHUR IN SELENIUM

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Summary—Determination of trace amounts of sulphur as Methylene Blue after reduction of sulphate to sulphide by hydriodic and hypophosphorous acids in acetic acid solution is applied to the determination of trace amounts of sulphur in selenium after removal of the selenium by evaporation with hydrobromic acid. Samples of 100 mg or less of selenium are chosen if the sulphur content is greater than 5–10 ppm; the time required for the separation is about 1·5 hr; 100 ppm of sulphur has been determined with a coefficient of variation of 5·2%. If the sulphur content is less than 5 ppm, 1-g samples must be taken and the time required is then about 3 hr; 0·4 ppm of sulphur has been determined with a standard deviation of 0·13 ppm. The accuracy of the method seems to be well within the random error.

THE importance of trace impurity effects in semiconductor materials is well known. Though most of the trace elements of interest can be determined with a fair degree of accuracy there seems to be a lack of good methods for as common a trace impurity as sulphur. This is perhaps best illustrated by the fact that such a modern and comprehensive monograph on trace methods as Koch and Koch-Dedic's *Handbuch der Spurenanalyse* completely omits the determination of sulphur.

Very few methods for determining trace amounts of sulphur in selenium have been described. Usually the procedures recommended are based on the turbidimetric determination of sulphur as barium sulphate. Separation of the dioxides of sulphur and selenium at 800°, followed by colorimetric determination of sulphur dioxide as described by Acs and Barabas[1] seems to be rapid but has some disadvantages. None of the methods is applicable to the determination of less than 3 μg of sulphur. The separation of selenium as selenium tetrabromide by means of a mixture of hydrobromic acid and bromine has also been mentioned, but if samples of more than 1 g must be taken this procedure is very time-consuming. A brief survey of methods for the determination of trace amounts of sulphur in selenium as well as of the demands for such analyses is given by Acs and Barabas.[1]

The determination of sulphur as Methylene Blue after reduction of sulphate to sulphide by hydriodic and hypophosphorous acids in acetic acid solution[2,3] is very sensitive. If a 10-cm cell is used 5 μg of sulphur can be determined with a standard deviation of 0·10 μg and 0·1 μg of sulphur with a standard deviation less than 0·03 μg. The great sensitivity of this method should make it well suited to the present purpose. It was found that the method was not applicable in the presence of selenium; hydrogen selenide is formed and oxidized to selenium in the absorption flask in contact with air. After separation of selenium as selenium tetrabromide, however, the results obtained were good. The sensitivity of the colour reaction allows small samples to be

used and the evaporation of selenium tetrabromide takes only 3 hr at most. The following procedure was adopted.

EXPERIMENTAL

Apparatus

The separation procedure is carried out in a 50-ml round-bottomed flask with conical B24 ground-glass joint, the flask being subsequently used for the reduction. The flask is placed in a sand-bath on a hot-plate with an infrared drying lamp (250 W) above and a cylinder of glass around it to accelerate the evaporation by preventing condensation in the neck of the flask (Fig. 1).

For the reduction Gustafsson used a round-bottomed flask with a spherical ground joint and a side-tube for introduction of nitrogen. We found it more convenient to use the commercially available flasks just mentioned and to introduce the nitrogen by means of a 9 mm o.d. tube through the lower part of the condenser and ending 1·0–2·5 mm above the bottom of the flask. The flasks were selected to give the right distance between the end of the tube and the bottom. The rest of the apparatus was strictly according to Gustafsson.

The light absorption is determined with a spectrophotometer. Measured at the wavelength stated by Gustafsson, 1·0 μg of sulphur in 100 ml of solution gives an absorbance of 0·154 at 20° in a 10-cm cell.

Reagents

The reduction and colour-reaction reagents are those described by Gustafsson.

Sodium chloride solution, 0·1%.

Nitric acid, conc.

Hydrobromic acid, 48%.

Distillation of the acids is necessary to remove traces of sulphur. After one distillation in a silica apparatus nitric acid gave a blank of 10 μg of sulphur/l. and hydrobromic acid a blank of 25 μg of sulphur/l. The distilled acids are preferably stored in silica flasks, but Pyrex flasks may be used if they are first boiled for 10 min with the reducing mixture.

Recommended procedure

It is very important to clean new round-bottomed flasks thoroughly immediately before use to remove traces of sulphur that may be present. Boil the flasks with 3 ml of the reducing mixture in the reduction apparatus for about 10 min. Rinse them with distilled water and with 6*M* hydrochloric acid and again with distilled water. After this treatment the flasks are ready for use.

The figures in parentheses below refer to 1-g samples. Transfer by pipette 1 ml of 0·1% sodium chloride solution into a 50-ml round-bottomed flask. Evaporate to dryness in a drying oven at 130°. Weigh out 100 mg (1 g) of selenium and transfer it to the flask. Add 1 ml (6 ml) of nitric acid, keeping the flask in a slanting position to prevent spattering losses during the violent reaction. Evaporate to dryness in a sand-bath on a hot-plate under an infrared drying lamp and with a cylinder of glass around the flask. The sand-bath is kept as hot as possible but splashing must be avoided. Add, and evaporate to dryness after each addition, 2 × 0·5 ml (5 + 1 ml) of hydrobromic acid, 0·5 ml (1 ml) of nitric acid and 0·5 ml (1 ml) of hydrobromic acid. After this treatment, which takes about 1½ hr (3 hr), the separation is complete and all the sulphur is left as sulphate. Cool to room temperature and proceed strictly according to Gustafsson with the few exceptions mentioned above under "apparatus". It has been found that the ground joints of the round-bottomed flasks need not be greased with silicone lubricant. Instead they are wetted with a few drops of the reducing mixture and thus the flasks are more easily kept clean. The nitrogen flow-rate is kept very low at the beginning of the reduction and not until the boiling point is reached (after about a minute) is it increased to about 150 ml/min.

By this procedure sulphur has been determined in some commercial selenium samples and in some selenium samples from Bolidens Aktiebolag (Tables I–III).

DISCUSSION

Procedure

It is important to keep the blank as low as possible. The total blank is composed of the blanks for the separation and reduction procedures and the colour reaction. The colour reaction in the absence of sulphide gives a blank corresponding to 0·25 μg of

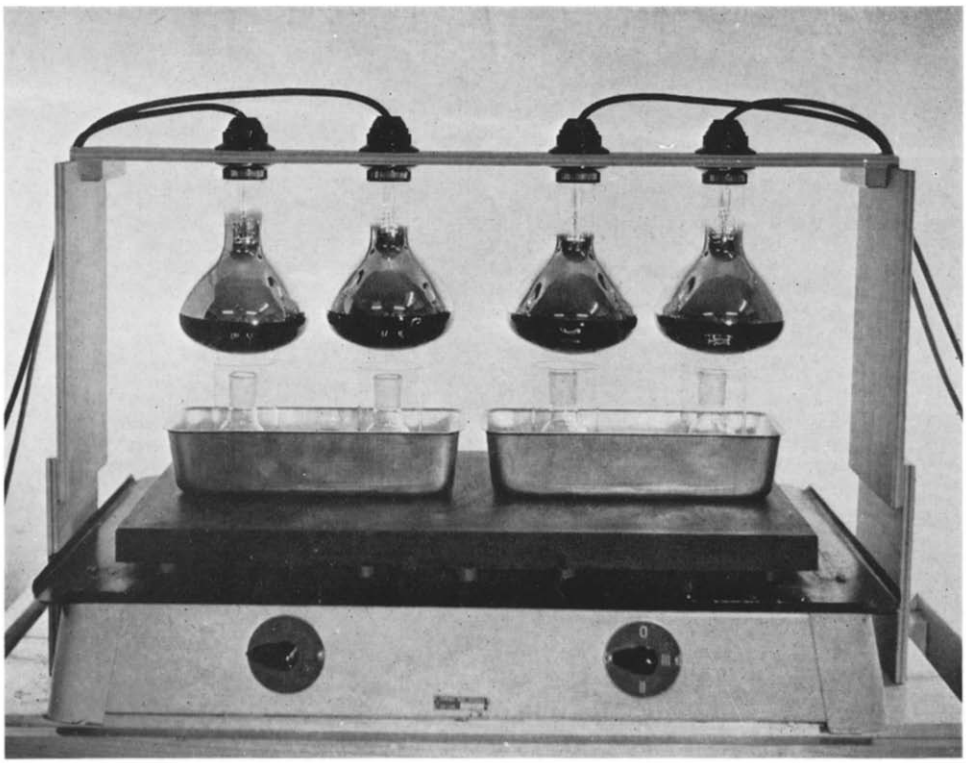

FIG. 1.—The apparatus used for the separation procedure. The equipment shown has been in use for more than a year.

sulphur. The yellow colour due to the iron(III) used as oxidant can be bleached by phosphoric acid but the absorbance at the wavelength used is unchanged. The reduction gave a blank corresponding to 0·11 μg of sulphur. The nitric and hydrobromic acids used for the separation of selenium gave blanks of about 10 and 25 μg of sulphur/l., respectively. The mean value for the total blank when working with 1-g samples thus corresponds to 0·61 μg of sulphur. The standard deviation amounts to 0·05 μg.

The blank increases with the amount of acid used for the oxidation and evaporation of selenium and also with the time required for the separation (because of the possibility of air-borne contamination with sulphur). Therefore it is necessary to use the smallest possible amounts of the acids for the separation and the procedure described above has turned out to be the best and the least time-consuming of those tried. It is also important to have a sufficiently high temperature during the evaporation of selenium tetrabromide. This is attained as described; the cylinder of glass around the flask accelerates the evaporation by preventing condensation in the neck of the flask and halves the time needed.

Sufficient sodium chloride must be added to avoid losses of sulphuric acid during the evaporation. The vapour pressure of sulphuric acid is high enough to cause losses even at steam-bath temperature.

The separation of selenium was first done with a mixture of hydrobromic acid and bromine but the same results were obtained by using hydrobromic acid only.

Cleaning

Chromic-sulphuric acid must never be used for cleaning, as traces of sulphuric acid remain in glassware even after rinsing thoroughly with 6*M* hydrochloric acid. The reduction gave a blank corresponding to 0·57–0·94 μg of sulphur if the round-bottomed flasks were cleaned with chromic-sulphuric acid, compared with the blank of 0·11 μg of sulphur obtained by boiling the flasks with the reducing mixture as mentioned under "recommended procedure".

Precision

According to Gustafsson, Beer's law is valid up to 20 μg of sulphur in 100 ml, and the standard deviation is 0·12 μg. This has been confirmed. For standards ranging from 5 μg down to 0·1 μg of sulphur the standard deviation varied from 0·10 to 0·03 μg. The precision of analysis is shown in Table I.

Accuracy

As the colour reaction is quite specific for sulphur, high systematic errors will only be obtained in the presence of sulphur impurities in reagents and glassware, but these should be compensated for by the blank.

Low results may be due to (*a*) mechanical losses on dissolving the sample, (*b*) losses as hydrogen sulphide or sulphur dioxide on dissolving the sample and (*c*) losses as sulphuric acid during the evaporations. The mechanical losses are calculated to be well within the precision of the method. To investigate the possible loss of sulphuric acid by evaporation, samples of selenium were analysed after addition of standard amounts of potassium sulphate (Table II). No losses were indicated.

TABLE I.—DETERMINATION OF SULPHUR IN SELENIUM

Sample	Weight, *mg*	No. of determinations	Sulphur found, *ppm*	Standard deviation	
				ppm	relative, %
S 3805*	99·5–105·1	15	342	8·0	2·3
S 3805*	49·5–51·8	6	353	6·2	1·8
A 5502*	98·9–100·1	3	73	0·5	0·7
B 44533*	100·7–101·3	3	614	1·8	0·3
M S59†	98·7–112·1	5	105	1·9	1·8
M S61†	104·3–112·0	5	84	1·6	1·9
M S63†	94·8–109·6	5	85	1·6	1·9
M S65†	102·3–112·4	5	8·8	0·6	6·8
MS 67†	98·6–108·6	4	9·6	0·5	5·2
1513 B†	884–1070	10	0·31	0·13	—
1702 A†	842–989	9	0·41	0·13	—

* 1-cm cuvette
† 10-cm cuvette

TABLE II.—RECOVERY OF SULPHATE ADDED TO SAMPLE S 3805

Weight of sample, *mg*	99·6–105·3	99·5–101·1
Sulphur added, *μg*	39·30	19·53
No. of determinations	12	7
Mean of sulphur recovered, *μg*	39·35	19·94
Standard deviation, *μg*	1·05	2·18

1-cm cuvette.

TABLE III.—DETERMINATION OF SULPHUR IN MIXTURES OF SAMPLES

Taken						Total S, *μg*	Sulphur found, *μg*	Difference, *μg*
1702 A		MS 63		MS 65				
mg	S, *μg*	*mg*	S, *μg*	*mg*	S, *μg*			
886	0·36	104·2	8·84			9·20	9·11	−0·09
892	0·37	110·1	9·34			9·71	9·55	−0·16
903	0·37	105·0	8·90			9·27	8·74	−0·53
896	0·37	103·1	8·74			9·11	9·06	−0·05
897	0·37			109	0·96	1·33	0·94	−0·39
910	0·37			97	0·85	1·22	1·07	−0·15
899	0·37			102	0·90	1·27	0·92	−0·35
899	0·37			97	0·86	1·23	1·04	−0·19

1-cm cuvette.

Possible losses due to (*b*) were investigated in two ways. It seems reasonable to assume that losses of hydrogen sulphide or sulphur dioxide will be proportionally greater for the dissolution of a large sample low in sulphur than in the opposite case, as the oxidizing conditions should be better the smaller the sample. If losses occur, the analysis of a mixture of a large sample of low-sulphur selenium with a small sample of high-sulphur selenium should give a lower result than that calculated from the two sulphur contents. The results of experiments performed are given in Table III. Losses of about $0{\cdot}24 \pm 0{\cdot}17$ *μg* of sulphur are indicated at a level of 1–10 ppm of

sulphur. In other experiments the gases formed during the dissolution were passed through a solution of bromine in conc. nitric acid, and this was then analysed for sulphur by the method described. It was found to contain 1 μg of sulphur after dissolution of 1 g of selenium with a sulphur content of 614 ppm, 0·5 μg at a content of 85 ppm and $<$0·1 μg at a content of 0·4 ppm. It therefore seems that the possible losses are well within the random errors.

Acknowledgements—This work was suggested by Professor Folke Nydahl. The author wishes to thank him for the facilities placed at her disposal and for many valuable discussions. Thanks are also due to Bolidens Aktiebolag who supplied her with several selenium samples.

Zusammenfassung—Schwefelspuren lassen sich nach Reduktion von Sulfat zu Sulfid mit Jodwasserstoff- und unterphosphoriger Säure in Essigsäure als Methylenblau bestimmen. Mit dieser Methode werden Schwefelspuren in Selen bestimmt nach Entfernung des Selens durch Abrauchen mit Bromwasserstoffsäure. Als Proben werden 100 mg oder weniger Selen gewählt, wenn der Schwefelgehalt über 5–10 ppm liegt. Die Abtrennung dauert etwa 1,5 h; 100 ppm Schwefel werden einem Variationskoeffizienten von 5,2% bestimmt. Ist der Schwefelgehalt kleiner als 5 ppm, so müssen 1 g-Proben genommen werden, die Abtrennung dauert dann etwa 3 h. 0,4 ppm Schwefel wurden mit einer Standardabweichung von 0,13 ppm bestimmt. Die Genauigkeit der Methode ist anscheinend durch statistische Fehler bestimmt.

Résumé—On applique le dosage de traces de soufre à l'état de bleu de méthylène après réduction du sulfate en sulfure par les acides iodhydrique et hypophosphoreux en solution dans l'acide acétique à la détermination de traces de soufre dans le sélénium après élimination du sélénium par évaporation avec de l'acide bromhydrique. On choisit des échantillons de 100 mg ou moins si la teneur en soufre est supérieure à 5–10 ppm; le temps nécessité pour la séparation est d'environ 1,5 h; on a dosé 100 ppm de soufre avec un coefficient de variation de 5,2%. Si la teneur en soufre est inférieure à 5 ppm, il faut prendre des échantillons de 1 g et le temps nécessité est alors d'environ 3 h; on a dosé 0,4 ppm de soufre avec un écart type de 0,13 ppm. La précision de la méthode semble bien se situer à l'intérieur de l'erreur de hasard.

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TETRACHLOROGALLATE(III) COMPLEXES WITH BASIC TRIPHENYLMETHANE AND DIPHENYLNAPHTHYLMETHANE DYESTUFFS

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Summary—A general survey is given of the properties of tetrachlorogallate(III) complexes with basic dyestuffs of the triphenylmethane and diphenylnaphthylmethane class; solvents for extraction, the absorption spectra and molar absorptivities, the optimum concentrations of the dyestuffs and of hydrochloric acid, the stability of the compounds and their composition are also described. Analytical methods for the determination of traces of gallium by means of many of these complexes are suggested.

THERE are already known some compounds formed by certain inorganic complex anions (*e.g.*, $SbCl_6^-$, $AuCl_4^-$, $GaCl_4^-$ etc) with organic cations such as ammonium, oxonium, diazonium, arsonium, stilbonium, phosphonium, selenonium and sulphonium which are generally colourless. These compounds can be extracted from aqueous solution by means of various organic solvents or solvent mixtures. For analytical purposes, however, it is better to make use of coloured organic cations, which will give strongly coloured compounds with inorganic complex anions, and can be used for the determination of some elements found as traces or impurities in ores, concentrates, industrial products, *etc.*

Of the organic cations capable of forming such coloured compounds, the present paper is concerned with basic dyestuffs with two or three amino groups, taken in combination with the tetrachlorogallate(III) ion, $[GaCl_4]^-$. The dyestuffs belong to the following classes.

Diaminotriphenylmethane dyes. Malachite Green 1 (Colour Index[1] Basic Green 4/42000; *N,N,N′,N′*-tetramethyl-4,4′-diaminotriphenylcarbinol chlorhydrate); Brilliant Green (C.I. Basic Green 1/42040; *N,N,N′,N′*-tetraethyl-4,4′-diaminotriphenylcarbinol sulphate); Astrazon Blue B (C.I. Basic Blue 5/42140; 4′,4″-diethylamino-3′,3″-dimethyl-3-chlorotriphenylcarbinol chlorhydrate).

Triaminotriphenylmethane dyes. Fuchsine (C.I. Basic Violet 14/42510; 4,4′,4″-triamino-3-methyltriphenylcarbinol chlorhydrate); New Fuchsine (C.I. Basic Violet 2/42520; 4,4′,4″-triamino-3,3′,3″-trimethyltriphenylcarbinol chlorhydrate); Methyl Violet (C.I. Basic Violet 1/42535; *N,N,N′,N″*-pentamethyl-*p*-rosaniline chlorhydrate); Crystal Violet (C.I. Basic Violet 3/42555; hexamethyl-4,4′,4″-triaminotriphenylcarbinol chlorhydrate); Ethyl Violet (C.I. Basic Violet 4/42600; hexaethyl-4,4′,4″-triaminotriphenylcarbinol chlorhydrate).

Diaminodiphenylnaphthylmethane dyes. Victoria Blue (C.I. Basic Blue 11/44040; *N,N,N',N'*-tetramethyl-4,4'-diamino-*N''*-phenyl-4-naphthylaminocarbinol chlorhydrate); Fanal Blue B Supra (C.I. Basic Blue 7/42595 *N,N,N',N'*-tetraethyl-4,4'-diamino-*N''*-ethyl-4-naphthylaminocarbinol chlorhydrate).

EXPERIMENTAL

The purity of the dyestuffs was determined by reduction with titanium(III) chloride in acidic medium,[2] in accordance with the reaction

$$X_3OH + 2TiCl_3 + 2HCl = 2TiCl_4 + X_3H + H_2O.$$

The purities were: Malachite Green 94·9%; Brilliant Green 93·0%; Astrazon Blue B 38·6%; Fuchsine 81·6%; New Fuchsine 83·3%; Methyl Violet 85·7%; Crystal Violet 97·4%; Ethyl Violet 88·0%, and Victoria Blue 66·8%.

Since Methyl Violet is a mixture of methylated *p*-rosaniline (tetra-, penta- and hexa-) having the pentamethyl derivative as main component, its purity was calculated on the basis of the pentamethyl derivative; one CH_3 group more or one less influences the result only to a small extent, and one compensates for the other.

For extraction, the optimum conditions are 2 ml of 2% solution of Malachite Green, Brilliant Green, Fuchsine, New Fuchsine, Methyl Violet, Crystal Violet or Ethyl Violet, or 0·5 ml of 2% Astrazon Blue B solution, added to 1 ml of gallium solution (10 μg of gallium) in 6*M* hydrochloric acid and diluted to 5 ml final volume, which is then extracted with 5 ml of solvent (Fig. 1). The optimum concentration of hydrochloric acid is 5·5–6*M*, irrespective of the cation, as shown in Fig. 2. It is essential to form the $[GaCl_4]^-$ anion and for this 6*M* hydrochloric acid is completely satisfactory.

The complex formed by the $[GaCl_4]^-$ anion and the cations of the basic diaminotriphenylmethane dyestuffs can be extracted from 6*M* hydrochloric acid with benzene, and especially with mixtures of benzene and chlorobenzene (4:1 or 1:1) or chlorobenzene and carbon tetrachloride (4:1). Chlorobenzene cannot be used alone as extraction solvent, even though it yields a large molar absorptivity, because the separation of the two layers requires a very long time, owing to the closeness of the specific gravities of chlorobenzene (1·107) and 6*M* hydrochloric solution. If toluene is used for the extraction low absorptivities are obtained, and carbon disulphide gives very small molar absorptivities for the extracts. Carbon tetrachloride extracts none of the compounds and chloroform extracts the

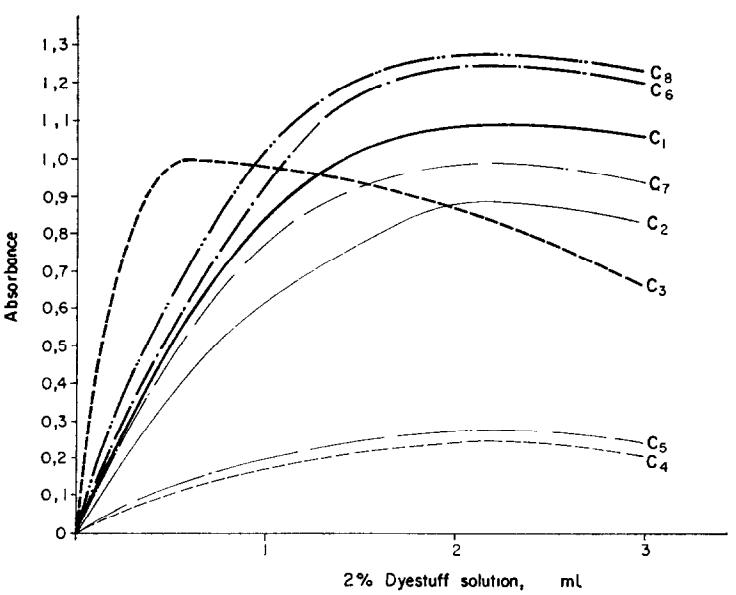

FIG. 1.—Effect of dyestuff concentration on absorbance of chlorogallate complexes. C_1—Malachite Green; C_2—Brilliant Green; C_3—Astrazon Blue; C_4—Fuchsine; C_5—New Fuchsine; C_6—Methyl Violet; C_7—Ethyl Violet; C_8—Crystal Violet.

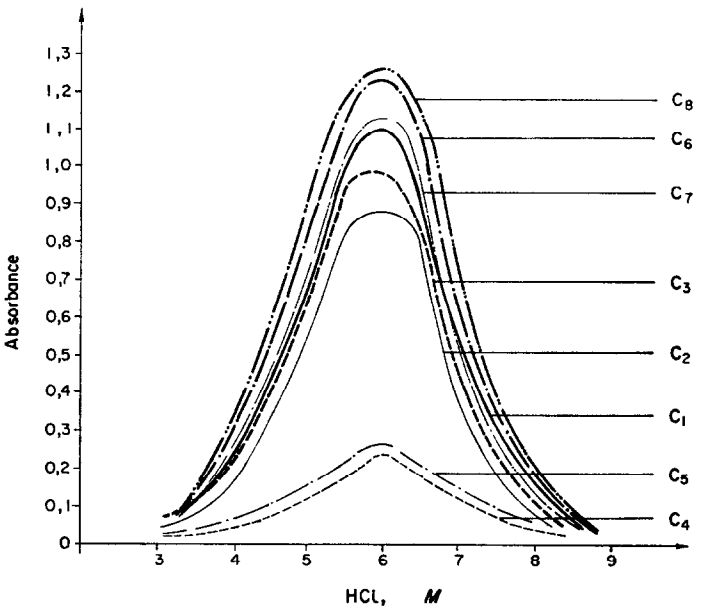

FIG. 2.—Effect of acidity on absorbance of chlorogallate complexes.
C_1—Malachite Green; C_2—Brilliant Green; C_3—Astrazon Blue; C_4—Fuchsine; C_5—New Fuchsine; C_6—Methyl Violet; C_7—Ethyl Violet; C_8—Crystal Violet.

dyestuffs as well as the $[GaCl_4]^-$ complexes. Of the complexes formed with the cations of the triaminotriphenylmethane class, those with Fuchsine and New Fuchsine are best extracted by a mixture of chloroform and cyclopentanone, and those of Methyl Violet, Crystal Violet or Ethyl Violet by chloroform alone or mixed with either acetone or acetylacetone. Benzene, toluene, carbon tetrachloride and carbon disulphide do not extract the chlorogallates of Methyl Violet, Crystal Violet and Ethyl Violet; chlorobenzene extracts them but only to a small extent. We have also tested 30 other organic solvents which, proved not to extract the chlorogallates.

The Victoria Blue chlorogallate is best extracted into benzene or a benzene–chlorobenzene mixture, and the Fanal Blue B Supra chlorogallate into chloroform–acetone or chloroform–acetylacetone mixtures. The presence of a naphthyl group instead of a phenyl group did not alter the behaviour toward organic solvents.

RESULTS

The molar absorptivities are given in Tables I, II and III, and the distribution ratios and degrees of extraction in Table IV.

For all determinations a correction was applied for a blank. Some of the molar

TABLE I

Solvent	Malachite Green chlorogallate 635 mμ	Brilliant Green chlorogallate 635 mμ	Astrazon Blue B chlorogallate 620 mμ
Benzene	38200	30500	34700
Toluene	27000	18900	5790
Chlorobenzene	64500	63100	65900
Carbon disulphide	3970	2160	1670
Benzene–chlorobenzene (4:1)	54800	50000	58400
Benzene–chlorobenzene (1:1)	62400	60400	65500
Chlorobenzene–carbon tetrachloride (4:1)	64200	62700	65700

TABLE II

Solvent	Fuchsine chloro-gallate 555 mμ	New Fuchsine chloro-gallate 555 mμ	Methyl Violet chloro-gallate 595 mμ	Crystal Violet chloro-gallate 589 mμ	Ethyl Violet chloro-gallate 592 mμ
Chlorobenzene	350	2330	6840	8230	7150
Chloroform	520	1740	16600	11300	11300
Chloroform–acetone (6:1)	2400	5760	43200	47400	33600
Chloroform–methyl ethyl ketone (6:1)	2580	6830	37600	40300	31700
Chloroform–methyl isobutyl ketone (6:1)	2160	3560	20900	26600	25500
Chloroform–cyclopentanone (6:1)	7540	9200	29600	31400	27300
Chloroform–cyclohexanone (6:1)	3070	4880	29600	25400	27300
Chloroform–acetylacetone (6:1)	2960	2970	44600	48800	35200

absorptivities are higher than those previously obtained (J. Jankovsky[3]—48800 for Malachite Green; Kuznetsova and Tananaeva[4]—29280 for Brilliant Green; Kuznetsova and Tananaeva[5]—4200 for Methyl Violet).

By the methods of continuous variations or of series of equimolecular solutions[6–11] we have established the molar ratio of the organic cation to the $[GaCl_4]^-$ anion. The molarities studied ranged from 10^{-3} to $10^{-4}M$ and led to the conclusion that the combining ratio is 1:1.[12–14]

The distribution ratio[15] (Table IV) ranges from 2·70 for the chlorogallate of Malachite Green to 1·05 for the chlorogallate of Fuchsine, for equal volumes of organic solvent and aqueous phase; the degree of extraction varies between 87·1 and 51·2%.

TABLE III

Solvent	Victoria Blue chlorogallate 630 mμ	Fanal Blue B Supra chlorogallate 605 mμ
Benzene	39700	—
Toluene	26100	—
Chlorobenzene	48700	6450
Carbon disulphide	6550	—
Chloroform	—*	10700
Benzene–chlorobenzene (4:1)	41700	—
Chlorobenzene–carbon tetrachloride (4:1)	44000	—
Benzene–chlorobenzene (1:1)	42700	—
Chloroform–acetone (6:1)	—	31000
Chloroform–methyl ethyl ketone (6:1)	—	29300
Chloroform–methyl isobutyl ketone (6:1)	—	19170
Chloroform–cyclopentanone (6:1)	—	24700
Chloroform–cyclohexanone (6:1)	—	25600
Chloroform–acetylacetone (6:1)	—	31500

* Blanks and solutions gave very high absorbances.

TABLE IV. DISTRIBUTION RATIO AND DEGREE OF EXTRACTION

Dyestuff	Distribution ratio	Extraction, %	Organic solvent
Malachite Green	2·70	87·0	benzene
Brilliant Green	1·12	52·9	benzene
Astrazon Blue B	1·08	51·9	benzene
	1·14	53·3	chlorobenzene–carbon tetrachloride (4:1)
Fuchsine	1·05	51·2	chloroform–cyclopentanone (6:1)
New Fuchsine	1·06	51·4	chloroform–cyclopentanone (6:1)
Methyl Violet	1·30	56·5	chloroform–acetone (6:1)
	1·36	57·6	chloroform–acetylacetone (6:1)
Crystal Violet	1·35	57·4	chloroform–acetone (6:1)
	1·48	59·7	chloroform–acetylacetone (6:1)
Ethyl Violet	1·46	59·3	chloroform–acetone (6:1)
	1·54	60·6	chloroform–acetylacetone (6:1)

CONCLUSIONS

All the compounds studied had absorption spectra with a well-defined maximum between 580 and 650 mμ (Fig. 3), in the best solvents given in Tables I–III.

The molar absorptivities are higher for the complexes with Methyl Violet and Crystal Violet, which possess methyl groups, than for those with Ethyl Violet, which has ethyl groups, and also with Malachite Green as compared with Brilliant Green. The highest molar absorptivity is obtained with Astrazon Blue B, which has methyl, ethyl and chlorine groups.

The compounds are stable in the organic phases for 6 hr for the Fuchsine and New Fuchsine complexes and 24 hr, for the others slightly decreasing thereafter. The

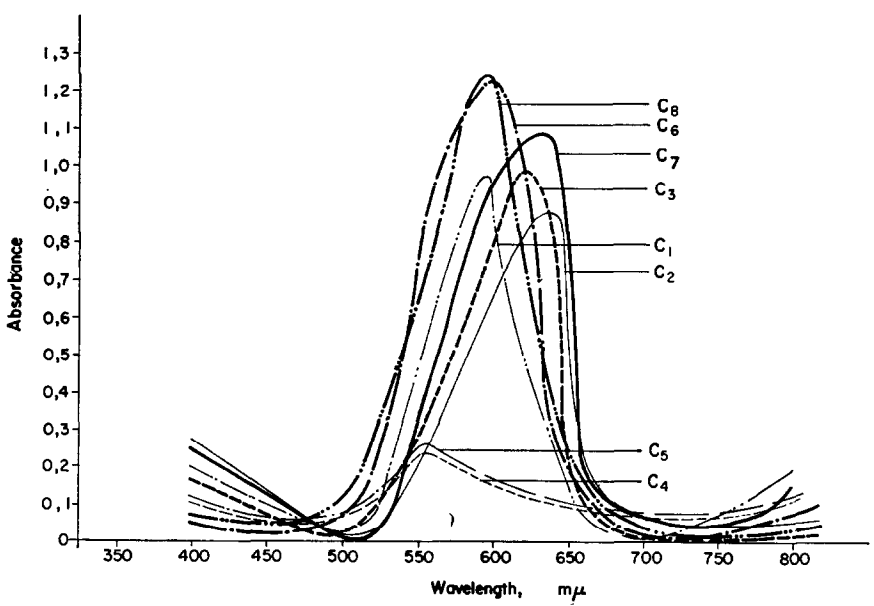

FIG. 3.—Absorption spectra of chlorogallates of various dyestuffs
C_1—Malachite Green; C_2—Brilliant Green; C_3—Astrazon Blue; C_4—Fuchsine; C_5—New Fuchsine; C_6—Methyl Violet; C_7—Ethyl Violet; C_8—Crystal Violet.

absorbance of the extracts increases linearly with the gallium concentration up to 15 μg of gallium in 5 ml of aqueous solution.

New methods have been developed from this work with Crystal Violet,[16] Astrazon Blue[17] and Victoria Blue for the determination of gallium in bauxite, nepheline syenite, zinc concentrates, by-products in the zinc industry, and coal-ash, either directly in the presence of other elements, or after separation of gallium from interfering elements. The results obtained are good and the time required for analysis is shorter than for the classical oxine method.

Zusammenfassung—Es wird ein allgemeiner Überblick über die Eigenschaften von Tetrachlorogallat(III)-komplexen mit basischen Farbstoffen der Triphenylmethan- und Diphenylnaphthylmethanreihe gegeben; Losungsmittel zur Extraktion, Absorptionsspektren und Extinktionskoeffizienten, optimale Konzentrationen von Farbstoffen und Salzsäure, Stabilität und Zusammensetzung der Verbindungen werden ebenfalls abgehandelt. Es werden analytische Verfahren zur Bestimmung von Galliumspuren mit vielen dieser Komplexe vorgeschlagen.

Résumé—On présente une étude d'ensemble des propriétés des complexes du tétrachlorogallate(III) avec les colorants basiques des groupes triphénylméthane et diphénylnaphtylméthane; on décrit également des solvants d'extraction, les spectres d'absorption et les coefficients d'extinction moléculaire, les concentrations optimales des colorants et de l'acide chlorhydrique, la stabilité des composés et leur composition. On suggère des méthodes analytiques pour le dosage de traces de gallium au moyen d'un grand nombre de ces complexes.

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ESTIMATION OF THE MINIMUM DETECTABLE CONCENTRATION AND OPTIMUM INSTRUMENTAL CONDITIONS IN PRECISION ABSORPTION SPECTROPHOTOMETRY OF SUBSTANCES IN THE CONDENSED PHASE

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Summary—An expression for the signal-to-noise ratio in precision absorption spectrophotometry of molecules in the condensed phase is derived and used to calculate the theoretical minimum detectable sample concentration, C_{mt}, and to predict the best instrumental condition for measurement. Single-beam and double-beam instruments are considered. The theoretically calculated values of C_{mt} for several organic molecules are compared with the practical minimum detectable sample concentrations, C_{mp}, which are those concentrations giving an absorbance of 0·002. As long as the source of radiation is intense, and the root-mean-square noise-to-signal ratio for incident radiation passing through the blank is known, then the expression for C_{mt} is extremely simple and easy to evaluate for any given substance whose molar absorptivity is known. The influence of instrumental parameters on the value of C_{mt} is evaluated, and only the monochromator slitwidth, the number of combined blank and sample signal measurements, and the frequency response bandwidth of the electrometer-readout system have any significant effect on the value of C_{mt} (for any given wavelength setting of the monochromator).

THE minimum detectable sample concentration in molecular absorption spectrophotometry is generally defined as that sample concentration resulting in an absorbance of 0·002.[1–3] However, it is well-known that scale-expansion techniques can be used in precision spectrophotometry,[4] to increase the sensitivity of measurement. If experimental conditions are such that the minimum detectable sample concentration is limited by the signal-to-noise ratio, then the approach of Winefordner *et al.*,[5–8] can be used to estimate the theoretical minimum detectable sample concentration and optimum instrumental conditions. Several instrumental systems for absorption spectrophotometry will be considered here, and these include: a single-beam system with a d.c. amplifier read-out (which is the system generally used for quantitative absorption spectrophotometric measurements, *e.g.*, the Beckman DU spectrophotometer), a single-beam system, chopper-modulated with a tuned a.c. amplifier (few examples of this system are used in molecular absorption spectrophotometry, although most atomic-absorption instruments are of this type), and a double-beam system with a differential or a.c. amplifier read-out.

THEORY

The theoretical minimum detectable sample concentration, C_{mt}.

The theoretical minimum detectable sample concentration, C_{mt}, has been defined[7,9–15] as that concentration producing a signal-to-noise ratio having a value

of $3\sqrt{2}/\sqrt{n}$, *i.e.*,

$$\frac{i_o - i_s}{\overline{\Delta i_T}} = \frac{3\sqrt{2}}{\sqrt{n}} \tag{1}$$

where i_o is the photo-anodic current, in amperes, due to radiation from the light source passing through the blank solution and striking the photo-cathode surface of the multiplier phototube, i_s is similarly defined for radiation which has just barely been attenuated by passage through a sample solution of minimum detectable concentration, $\overline{\Delta i_T}$ is the total root-mean-square (r.m.s.) noise due to all sources, *e.g.*, shot noise, source flicker noise, and electrometer-amplifier noise, and n is the number of pairs of blank and sample measurements. The total r.m.s. noise can be experimentally determined by measuring the peak-to-peak noise and dividing by 5.[16,17] The limiting detectable signal-to-noise ratio expression takes on additional meaning if one considers that a signal which is $3\sqrt{2}/\sqrt{n}$ times greater than the total rms noise can be measured with about 99·7% confidence (for $n \geqslant 4$).

Signal-to-noise ratio for single-beam system with d.c. amplifier read-out

The instrumental system under consideration consists of a source, *e.g.*, a hydrogen arc-lamp for the ultraviolet region or a tungsten lamp for the visible–near infrared region, a monochromator with equal entrance and exit slitwidths (*e.g.*, a Beckman DU, with suitable entrance optics), a multiplier-phototube, a d.c. electrometer-amplifier, and a read-out device, *e.g.*, a meter or recorder.

The photo-anodic currents i_o and i_s are given[5,6] by

$$i_o = \gamma k_m W s I^\circ, \tag{2}$$

and

$$i_s = \gamma k_m W s I^\circ \exp(-2{\cdot}3abC). \tag{3}$$

Near the theoretical minimum detectable sample concentration, C_{mt}, i_s is given by

$$i_s = \gamma k_m W s I^\circ(1 - 2{\cdot}3abC_{mt}). \tag{4}$$

The symbols in equations (2), (3) and (4) are defined as follows:

γ = photo-anodic sensitivity factor, in amperes produced at the anode of the photodetector per watt of light striking the photocathode
k_m = monochromator factor = $HT_t\Omega/m^2$, cm.ster
m = entrance optics factor to account for magnification of source image focused on slit
H = height of exit and entrance slit of monochromator, cm
T_t = transmittance factor of monochromator and entrance and exit optics
Ω = solid angle of incident radiation subtended by the monochromator, in steradians (usually Ω is the ratio of the effective collimator area or the area of the dispersing device, A_c, divided by the square of the focal length, F, of the collimator)
W = slitwidth of monochromator, cm
$s = R_d W$, mμ
I° = intensity of continuous source, W.cm^{-2}.ster^{-1}.mμ^{-1}
R_d = reciprocal linear dispersion of the monochromator, mμ.cm^{-1}
a = molar absorptivity, l.mole^{-1}.cm^{-1}

b = thickness of absorbing layer, cm
C = concentration of sample solution, mole.l.$^{-1}$
C_{mt} = theoretical minimum detectable sample concentration, mole.l.$^{-1}$.

By subtracting equation (4) from equation (2), the absorption signal at the theoretical minimum detectable sample concentration, C_{mt}, is given by,

$$(i_o - i_s)_{C_{mt}} = 2{\cdot}3abC_{mt}\gamma k_m WsI^\circ. \tag{5}$$

The total rms noise signal, $\overline{\Delta i_T}$, is a result of shot noise in the phototube, $\overline{\Delta i_P}$, flicker noise in the continuous source, $\overline{\Delta i_F}$, and amplifier-electrometer noise, $\overline{\Delta i_E}$. Because these noises are independent of each other, they add quadratically[5,6] and therefore $\overline{\Delta i_T}$ is given by

$$\overline{\Delta i_T} = \sqrt{\overline{\Delta i_P}^2 + \overline{\Delta i_F}^2 + \overline{\Delta i_E}^2}. \tag{6}$$

The phototube shot noise current, $\overline{\Delta i_P}$, in amperes at the anode, is given[5,6,18] by

$$\overline{\Delta i_P} = \sqrt{k_D(i_t + i_o)\Delta f}, \tag{7}$$

where:

k_D = detector factor = $2eBM$, coulombs
e = charge of electron, coulombs
B = factor to account for secondary emission of electrons in the phototube[18]
M = total gain of the phototube
i_t = thermionic emission anodic current in the phototube, in amperes (the dark current)
Δf = frequency-response bandwidth of the electrometer-amplifier–read-out system,[18] sec^{-1}.

If i_o from equation (2) is substituted into equation (7), then

$$\overline{\Delta i_P} = \sqrt{k_D(i_t + \gamma k_m WsI^\circ)\Delta f}. \tag{8}$$

The r.m.s. flicker noise signal due to flicker in the continuous source, in amperes at the photo-anode, is given[6] by

$$\overline{\Delta i_F} = \chi\sqrt{\Delta f}\, i_o = \chi\sqrt{\Delta f}\,\gamma k_m WsI^\circ \tag{9}$$

where χ is the r.m.s. fluctuation in the intensity of the source, $\overline{\Delta I^\circ}$, compared to the source intensity, I°, *i.e.*, $\chi = \overline{\Delta I^\circ}/I^\circ$ for a 1-Hz frequency-response bandwidth, and has units of sec$^{1/2}$.

The r.m.s. noise signal due to the electrometer–amplifier, in amperes at the photo-anode, is given[5] by

$$\overline{\Delta i_E} = \zeta\sqrt{\Delta f}\,(i_t + i_o) = \zeta\sqrt{\Delta f}\,(i_t + \gamma k_m WsI^\circ), \tag{10}$$

where ζ is the fraction of the total current $(i_t + i_o)$ which results in a noise for a 1-Hz frequency-response bandwidth, and has units of sec$^{1/2}$.

The total r.m.s. noise signal, in amperes at the read-out, $\overline{\Delta i_T}$, is therefore given by

$$\overline{\Delta i_T} = \{k_D\,\Delta f(i_t + \gamma k_m WsI^\circ) + \Delta f[(\chi\gamma k_m WsI^\circ)^2 + \zeta^2(i_t + \gamma k_m WsI^\circ)^2]\}^{1/2}. \tag{11}$$

The signal-to-noise expression, $(i_o - i_s)/\overline{\Delta i_T}$ at the theoretical minimum detectable

sample concentration, C_{mt}, can be found by dividing equation (5) by equation (11), and setting the quotient equal to the right hand term in equation (1).

$$\frac{3\sqrt{2}}{\sqrt{n}} = \left(\frac{i_o - i_s}{\overline{\Delta i_T}}\right)_{C_{mt}} = \frac{2 \cdot 3abC_{mt}\gamma k_m WsI^\circ}{\sqrt{\{k_D \Delta f(i_t + \gamma k_m WsI^\circ) + \Delta f[(\chi\gamma k_m WsI^\circ)^2 + \zeta^2(i_t + \gamma k_m WsI^\circ)^2]\}}}. \quad (12)$$

Signal-to-noise ratio for single-beam system with a.c. amplifier read-out

The system under consideration is assumed to be identical to the single-beam system with d.c. amplifier read-out with the exception that the light source is modulated, and an a.c. amplifier tuned to the chopper frequency is used. The equations for the absorption signal and noise are essentially identical to those derived for d.c. operation except that the source intensity is reduced by a factor t, for the decrease in source intensity due to the chopper. Usually t will be 1/2 and so the intensity of the source, which must be introduced into the signal and noise expressions, is $I^\circ/2$, where I° is the intensity of the unmodulated continuous source. In addition, since only alternating signals are amplified and the thermionic current, i_t, is a d.c. current, the electrometer noise expression, $\overline{\Delta i_E}$, does not contain i_t.

Signal-to-noise ratio for double-beam system with a.c. amplifier read-out

The system under consideration is basically the same as the single-beam a.c. system except that the optics are usually arranged to pass a double beam through the optical system, and so only one phototube is needed. Such a system provides higher accuracy than instruments that split the beam after it has passed through the optical system, and require two phototubes. When two phototubes are needed, errors result because of lack of balance due to different drift rates in the two phototubes. If the phototubes are well-matched, then either system can be dealt with by the expressions derived here. Of course, it should be pointed out that generally double-beam systems are used for qualitative studies, and single-beam systems are used for routine quantitative analyses. However, if the following conditions are met, then the expressions derived for the single-beam system with d.c. amplifier read-out will be approximately valid except that the i_t term in the electrometer noise term can be omitted: the two cells (and phototubes if two are used) must be matched or their difference compensated for; no systematic or random errors other than those already considered must arise when the beam is passing through one cell; the phototube, source flicker, and electrometer-amplifier noises must be the only ones which are significant.

Optimization of instrumental conditions

The optimum value of any instrumental parameter, X, for measuring the theoretical minimum detectable sample concentration, C_{mt}, can be found in the usual way by differentiating the expression for C_{mt} with respect to X, equating to zero, and solving

$$\frac{dC_{mt}}{dX} = 0. \quad (13)$$

The slitwidth, W. By this procedure it is found that there is no optimum slitwidth for either a single- or a double-beam system, *i.e.*, a plot of C_{mt} *vs.* W indicates that C_{mt} decreases with increasing W until a minimum plateau is reached (Fig. 1); it is assumed in this and all other cases in this paper that the spectral bandwidth of the monochromator is considerably smaller than the half-intensity width of the absorption band—this is generally the case in ultraviolet–visible absorption spectrophotometry. However, even though no optimum slitwidth exists for molecular absorption spectrometry, there is an analytically useful slitwidth, W_u, which is defined as that slitwidth above which

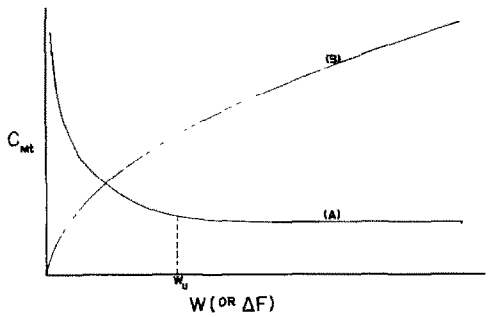

FIG. 1.—Typical plots of C_{mt} *vs.* W (Curve A) and C_{mt} *vs.* Δf (Curve B).

less than a 10% change in C_{mt} results with increase in slitwidth; it is assumed that the spectral band-width $R_d W_u$ covers only the absorption band being studied and does not exceed ~20% of the halfwidth of the absorption band.

The frequency-response bandwidth, Δf. Theoretically there is no optimum value of Δf (Fig. 1.); a plot of C_{mt} *vs.* Δf indicates that C_{mt} will decrease without limit as Δf is decreased. The frequency-response bandwidth can be decreased by use of an integration device or a time-averaging technique. However, it is seldom practical to use integration times much longer than 5 sec, because of drift in the light source or electronic system, and generally a time constant of about 1 sec is used.

Other instrumental parameters. No other instrumental parameters can be optimized in molecular absorption spectrophotometry. Indeed, of the other instrumental parameters, only phototube voltage is generally variable, and it is well-known that the signal-to-noise ratio (and hence C_{mt}) does not vary with phototube voltage as long as the voltage is sufficient to give a detectable signal and noise, and is below that at which regenerative ionization occurs in the phototube.

The theoretical minimum detectable sample concentration

Solving for C_{mt} from equation (12) results in

$$C_{mt} = \frac{1{\cdot}84\sqrt{k_D \Delta f (i_t + \gamma k_m W s I^\circ) + \Delta f [(\chi\gamma k_m W s I^\circ)^2 + \zeta^2 (i_t + \gamma k_m W s I^\circ)^2]}}{ab\gamma k_m W s I^\circ \sqrt{n}}, \tag{14}$$

for a single-beam d.c. electrometer-amplifier system. For a single- or double-beam a.c. electrometer–amplifier system, i_t drops out of the electrometer noise term in equation (14), and for the single-beam a.c. system, I° must be replaced by $I^\circ t$.

Now if the signal due to the light source is much greater than the value of i_t and if the slitwidth is set to some value near to or greater than W_u, then the shot noise term can be neglected, and the expression for C_{mt} can be greatly simplified, *i.e.*,

$$C_{mt} = \frac{1{\cdot}84\sqrt{\Delta f(\chi^2 + \zeta^2)}}{ab\sqrt{n}}. \tag{15}$$

Equation (14) can also be written as

$$C_{mt} = \frac{1{\cdot}84\overline{\Delta i_T}}{abi_0\sqrt{n}}, \tag{16}$$

where $\overline{\Delta i_T}/i_0$ is the ratio of r.m.s. noise to the signal due to radiation passing through the blank solution and is experimentally measurable. Equation (16) is very simple to evaluate and can be used even if the individual noise flicker factors χ and ζ are not known.

Practical minimum detectable sample concentration

The experimentally practical minimum detectable sample concentration, C_{mp}, can be[1–3] defined as that concentration resulting in an absorbance of 0·002, *i.e.*,

$$C_{mp} = \frac{0{\cdot}002}{ab}. \tag{17}$$

The limiting value of 0·002 is chosen on the basis of the smallest readable transmittance value on a null-type spectrophotometer. Of course, if the signal-to-noise ratio reaches the value given in equation (1) at absorbances greater than 0·002, then $C_{mt} > C_{mp}$, and the C_{mp} values will be erroneous. Usually, however, the signal-to-noise ratio will reach the value given in equation (1) at absorbances smaller than 0·002, and so $C_{mt} < C_{mp}$; in this case the sensitivity can be improved by scale expansion (as long as the conditions mentioned for C_{mt} are met).

EXPERIMENTAL

Measurement of the theoretical minimum detectable sample concentration, C_{mt}, can only be achieved experimentally if the transmittance scale is expanded electronically (precision spectrophotometry)[4] so that the transmittance reading error is negligible, and the instrumental noises are observable and significant.

Apparatus

A Beckman DU monochromator with hydrogen arc and tungsten filament lamps and power supply was used for all measurements. The Beckman amplifier system was not used. Instead, the output of a IP28 RCA multiplier phototube was fed directly into a high sensitivity electrometer (Model 610 BR, Keithley Instruments, Inc., Cleveland, Ohio). The electrometer output was detected by means of a potentiometric recorder (Model SR, E. H. Sargent and Co., Chicago, Ill.). The multiplier phototube was powered by a well-regulated power supply (Model 240, Keithley Instruments, Inc.).

The change in electronics was needed to achieve accurate measurements of signal-to-noise ratios. The separate phototube power supply set at a single voltage was used to minimize erratic phototube behaviour resulting from variations in the photo tubevoltage (the sensitivity on the null-type Beckman DU spectrophotometer is varied by changing the phototube voltage, whereas in our system the sensitivity was varied by changing the imput load resistor of the electrometer). To avoid errors due to mismatch or misalignment of the blank and sample cells, the cells used were selected to give a match within 1% on the tenfold expanded scale even when they were shifted into and out of position for measurement. The measurement electronics and hydrogen lamp used as light source were allowed to warm up for at least 1 hr before to minimize drift of the source radiance. To eliminate any small

errors due to drift in the light source, measurements of blank and sample signals were taken within 2 min of each other.

Reagents

The compounds used in this study were reagent grade and were phenanthrene,1,2-benzanthracene, and *p*-nitrophenol. Solutions of these compounds varying in concentrations from 10^{-1}–$10^{-10}M$ were prepared by successive dilution with ethanol. Absolute ethanol was distilled through a 6-ft vacuum-jacketed and silvered column with a reflux ratio of 20:1. The column was packed with 3/8-in. coil helices. Only the middle fraction was used.

RESULTS AND DISCUSSION

The values of the instrumental and spectral parameters used in equation (14) are listed in Table I. The molar absorptivities, a, for the compounds studied were calculated from the slopes of absorbance *vs.* concentration plots. The flicker factors, χ and ζ, were measured with *no* sample cell in the light beam. These values were used in equation (15) to calculate the theoretical minimum detectable sample concentrations C_{mt} [identical values of C_{mt} result from use of equation (14)]. Experimentally

TABLE I.—MEASURED VALUES OF EXPERIMENTAL PARAMETERS AND COMPARISON OF THEORETICAL (C_{mt}) AND PRACTICAL (C_{mp}) MINIMUM DETECTABLE SAMPLE CONCENTRATIONS FOR THREE ORGANIC COMPOUNDS*

Compound	λ, $m\mu$	a	γ, A/W	I°, $W/cm^2.ster.m\mu$	R_d, $m\mu/cm$	W_u, mm	C_{mt}, M	C_{mp}, M
Phenanthrene	250	7×10^4	$2{\cdot}15 \times 10^4$	$2{\cdot}6 \times 10^{-6}$	18·5	0·40(0·05)†	$8{\cdot}8 \times 10^{-9}$	$2{\cdot}9 \times 10^{-8}$
1,2-Benzanthracene	286	3×10^5	$3{\cdot}4 \times 10^4$	$1{\cdot}2 \times 10^{-6}$	29·5	0·60(0·06)†	$2{\cdot}1 \times 10^{-9}$	$6{\cdot}7 \times 10^{-9}$
p-Nitrophenol	312	1×10^4	$4{\cdot}1 \times 10^4$	$7{\cdot}7 \times 10^{-7}$	42·5	0·40(0·05)†	$6{\cdot}2 \times 10^{-8}$	$2{\cdot}0 \times 10^{-7}$

* Values of other measured instrumental parameters are as follows: $n = 4$; $k_m = (HT_t\Omega)/m^2 = 1{\cdot}0 \times 10^{-3}$ cm.ster; $b = 1{\cdot}00$ cm; $BM = 3{\cdot}51 \times 10^6$; $i_t = 9{\cdot}6 \times 10^{-11}$ A; $\Delta f = 1$ sec^{-1}. The evaluation of these parameters and of γ and I° is described by Cetorelli and Winefordner.[18] The values of χ and ζ were measured as described and were both approximately 5×10^{-4} sec$^{1/2}$. The value of e is $1{\cdot}6 \times 10^{-19}$ C.

† Values in parentheses are for the full intensity of the lamp. The other values were used when a neutral density filter was used to attenuate the intensity.

measured values of C_{mt} [obtained by using equation (1)] agreed with the calculated values to within $\pm 15\%$. This demonstrates that systematic and random errors due to cells and cell positioning were negligible (the major source of error is in the flicker factors, which are measured to about $\pm 15\%$).

Calculated values of C_{mt} and C_{mp} are given in Table I. The value of n, equation (1), was arbitrarily taken to be 4. Of course, if more measurements of the sample and blank signals are made, n is increased and C_{mt} will be even smaller although the rate of decrease of C_{mt} with increase in n is slow for $n > 10$. It should also be noted that the values of C_{mt} in Table I are all lower than the C_{mp} values and therefore if well-matched cells and experimental techniques are used, the theoretical minimum detectable sample concentrations can be measured confidently if scale expansion techniques are used.

It was experimentally verified that the signal-to-noise ratio (and C_{mt}) was essentially independent of the applied phototube voltage (as long as the voltage was below the point of regenerative ionization). Therefore the same signal-to-noise ratio and the same sensitivity of measurement are obtained over a wide range of applied phototube voltages. This result is of significant interest when it is realized that some instruments, *e.g.*, the Beckman DU, control the instrumental sensitivity by simply varying the phototube voltage.

It is also interesting to note that essentially the same value of W_u results for all wavelengths in the ultraviolet–visible region. This would seem to indicate that a monochromator with fixed slits, about W_u in width, would be quite ideal for quantitative spectrophotometric measurements and should be relatively inexpensive to purchase. Again it should be stressed that it is assumed that the spectral bandwidth corresponding to W_u, *i.e.*, $s = R_d W_u$, is assumed to be much smaller than the half-intensity width of the absorption band of the species being measured. Fortunately the value of W_u is near W_{min}, the minimum resolving-power slitwidth of the monochromator[19], and so good spectral resolution should also be obtained. Of course, if a more intense source were used, then W_u would be even smaller, and closer to W_{min}, and in fact C_{mt} would be independent of W_u, *i.e.*, if I° is large, then the phototube (shot) noise is insignificant compared to the other noises [see equation (15)]. It should also be noted that at high values of I°, the ratio $\overline{\Delta i_T}/i_0$ in equation (16) is constant for all wavelengths and phototube voltages. Therefore, C_{mt} for two different compounds under the same instrumental conditions is dependent *only* on the other absorptivity, a.

The smallest useful value of C_{mt} which can be used with confidence will result when the wavelength of the monochromator is adjusted to the absorption peak for which a is maximum, Δf is about 0·1 sec^{-1}, n is about 10, and the monochromator slitwidth is $\geqslant W_u$. With a given instrumental system, it is difficult to vary χ and ζ but if a more stable system were used such that χ and ζ were smaller, then C_{mt} would, of course, be smaller.

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Zusammenfassung—Es wird ein Ausdruck für das Signal-Rausch-Verhältnis bei der Präzisions-Absorptionsspektrophotometrie von Molekülen in kondensierter Phase abgeleitet und zur Berechnung der theoretisch nachweisbaren Mindestkonzentration und zur Ermittlung der besten apparativen Meßbedingungen verwendet. Ein- und Zweistrahlgeräte werden berücksichtigt. Die theoretisch berechneten C_{mt}-Werte mehrerer organischer Moleküle werden mit den praktischen Nachweisgrenzen C_{mp} verglichen, das sind die Konzentrationen, die die Extinktion 0,002 geben. Solange die Strahlungsquelle intensiv genug und die Wurzel aus dem mittleren Signal-Rausch-Verhältnisquadrat der durch die Referenzlösung einfallenden Strahlung bekannt ist, ist der Ausdruck für C_{mt} sehr einfach und für jede Substanz mit bekanntem Extinktionskoeffizienten leicht zu berechnen. Der Einfluß apparativer Parameter auf C_{mt} wird ermittelt; nur die Spaltbreite am Monochromator, die Anzahl der Ablesungen für Probe- und Referenz-lösung und die Frequenz-Bandbreite des elektrischen Anzeigesystems haben einen wesentlichen Einfluß auf C_{mt} (bei einer gegebenen Wellenlängen-Einstellung am Monochromator).

Résumé—Une expression pour le rapport signal-bruit dans la spectrophotométrie d'absorption de précision de molécules en phase condensée a été établie et utilisée pour calculer la concentration minimale théorique détectable de l'échantillon ainsi que pour prévoir les meilleures conditions instrumentales pour la mesure. On considère les instruments à simple et double faisceau. On compare les valeurs théoriquement calculées de C_{mt} pour différentes molécules organiques aux concentrations minimales d'échantillon pratiquement détectables C_{mp}, qui sont les concentrations donnant une absorbance de 0,002. Tant que la source de radiation est intense, et que le rapport signal-bruit efficace est connu pour la radiation incidente passant à travers le témoin, l'expression de C_{mt} est extrêmement simple et aisée à évaluer pour

n'importe quelle substance donnée dont le coefficient d'extinction molaire est connu. On évalue l'influence des paramètres instrumentaux sur la valeur de C_{mt} et seuls la largeur de la fente du monochromateur, le nombre de mesures combinées de signaux témoin et essai et la largeur de la bande de réponse de fréquence du système d'électromètre de lecture ont un effet significatif sur la valeur de C_{mt} (pour n'importe quelle position de longueur d'onde donnée du monochromateur).

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INORGANIC POLAROGRAPHY IN ORGANIC SOLVENTS—III*

ANALYTICAL APPLICATIONS OF METAL–ACETYLACETONATE COMPLEXES IN TOLUENE

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Summary—Indium and palladium are determined polarographically with a dropping mercury electrode in a toluene phase, following extraction as the acetylacetonates from aqueous solutions containing 2–10 ppm of the metals (or 0·1–0·5 ppm with a greater ratio of sample volume to solvent volume). Of 31 elements examined, only Co(III), Cr(III), Cu(II), Fe(III), In, Mo(VI), Pd and Ti(IV) gave extractable complexes with reduction waves in the available potential range. Specificity for palladium is obtained by extraction at pH 0·5, and for indium at pH 9 in the presence of cyanide and ascorbic acid as masking agents.

THERE are few successful practical applications of inorganic polarography in organic solvents, and even fewer determinations in an organic phase following solvent extraction. They include the extraction of bismuth, antimony, copper, thallium, lead and indium diethyldithiocarbamates into chloroform,[1,2] the extraction of the 8-hydroxyquinoline and salicylaldoxime complexes of copper and lead[3] and the extraction of beryllium as the acetylacetonate.[4] The base electrolytes in these determinations were added in large excesses of some other solvent medium—methyl cellosolve/water, acetic acid, and dimethylsulphoxide respectively.

There has been no systematic study of complexes in organic solvents, and no attempt to use a simple generally applicable supporting electrolyte. Such studies would undoubtedly alleviate many of the problems associated with the aqueous polarography such as resolution of waves, sensitivity limitations and the effect of solution composition on half-wave potentials and diffusion currents.

Although masking agents may improve the resolution they often give rise to difficulties by causing a further change in the solution composition. In addition, most are too unselective in their action, and some of the more useful form complexes which are insoluble in water. A solvent extraction followed by polarography overcomes most of these difficulties by providing a solution of standard composition to which only a base electrolyte need be added to increase the conductivity of the solution. Selectivity can be obtained by suitable choice of solvent system, and an increase in sensitivity is possible through the extraction step.

Previous communications in this series[5,6] have dealt with ion-association systems, and it is the purpose of this paper to discuss the analytical applications of a chelating agent—acetylacetone. The poor selectivity of its reactions, the solubility of its complexes in organic solvents, and the negative potential at which it is itself reduced at the DME,[7] suggested that a polarographic examination would be worthwhile.

* Part II—*Talanta* 1967, 14, 239.

EXPERIMENTAL

Apparatus

An Elliot Polarograph Model 200 was used, with a dropping mercury electrode. Unless otherwise stated, the following operating conditions were used: potential sweep, 0·5 V/100 sec, drop time 4·1 sec, height of mercury reservoir 70 cm, mercury flow-rate 2·42 mg/sec, temperature 18° (approx), no damping or counter-current. An internal mercury pool anode was used, and samples were de-aerated by bubbling oxygen-free nitrogen through them. A mercury seal was used to prevent re-absorption of oxygen.

Reagents

Indium. Dissolve 0·5741 g of the metal in 5 ml of concentrated hydrochloric acid, and dilute to 500 ml. The solution is $10^{-2}M$.

Palladium. Dissolve 0·8866 g of the chloride in 10 ml of concentrated hydrochloric acid, and dilute to 500 ml. This is also $10^{-2}M$.

Acetylacetone. This was purified by the method of Steinbach and Freiser[9]—shake 1 l. of general purpose grade reagent with 100 ml of dilute ammonia (1 + 10) and then with two 100-ml portions of distilled water. Distil, and collect the fraction boiling at 136°. A 0·1*M* solution in toluene was used.

Lithium chloride. A 0·5*M* solution in methanol, prepared from the dried salt.

Buffer solution pH 9.

Complexes of Co(II), Co(III), and Cr(III) were prepared according to the methods of Starý.[8]

Extractions

Equal volumes (30 ml) of 0·1*M* acetylacetone solution in toluene and of an aqueous solution containing 2 ml of $10^{-2}M$ metal ion solution and 5 ml of $10^{-2}M$ aqueous acetylacetone (to prevent precipitation of metal hydroxides) were shaken together. The pH was controlled by the addition of acetic acid or ammonia solution, and checked with a pH-meter. The aqueous and organic phases were not mutually presaturated before equilibration, as the volume changes were negligible. After being shaken for about 1 min the two phases were allowed to separate. The organic phase was then transferred to a 50-ml standard flask containing 10 ml of 0·5*M* lithium chloride in methanol, and diluted to the mark with methanol. A 5-ml portion was transferred to the polarographic cell, along with mercury for the anode-pool, and deoxygenated for 5 min. Polarograms were recorded at an instrument sensitivity of 10 μA/full-scale deflection, over the available potential range.

Toluene was chosen as solvent because chloroform is too easily reduced at the dropping mercury electrode,[5] and benzene is toxic. Otherwise the conditions are those given by Starý.[8]

RESULTS

Polarographic behaviour of various metal ions in acetylacetone-toluene-methanol solutions

Table I shows the half-wave potentials of the polarographic waves obtained in the organic and in the aqueous phases after extraction. An examination of the aqueous phase after extraction with toluene showed that Cr(III), Cu(II), Mo(VI), and Ti(IV) were incompletely extracted, in agreement with the results of other workers.[8] Many of the elements which did not give waves were nevertheless extracted to some extent, which illustrates the increase in selectivity which can be obtained by the combination of solvent extraction and polarography. Of the ions extracted under the conditions described, waves were obtained only for the following: Cu(II), Fe(III), In, Mo(VI), Pd, and Ti(IV), because the formation of the complexes of Co(III), Cr(III) and Mn(III) requires special conditions, and the extraction equilibria for these and for Mo(VI) are reached very slowly. In consequence, it was decided to investigate more fully the reduction of indium and of palladium acetylacetonates and to develop selective methods for the determination of these metals. The development of methods for the determination of Cu(II) and Fe(III) was not considered worthwhile in view of the already large number of satisfactory methods for these elements. These preliminary findings were checked by using benzene as solvent, and similar results were obtained.

Determination of Indium and Palladium

Extraction pH

A series of solutions containing the metals, and covering the pH range 0–10 were prepared, extracted, and examined as already described. The polarograms obtained showed that the extraction was quantitative over the whole range for palladium, but

TABLE I.—POLAROGRAPHIC EXAMINATION OF METAL-ACETYLACETONATES EXTRACTED INTO TOLUENE

Metal ion	pH of aqueous phase	$E_{1/2}$ Aqueous phase after extraction, *V*	$E_{1/2}$ Organic phase after extraction, *V*
——	4, 6, 8, 10	−1·3	−1·45
Ag	7	>0·0	—
Al	7	—	—
As(V)	2	Two coincident waves between −0·26 and −0·60	—
Be	6	—	—
Bi	2	>0·0	—
Cd	7	−0·60	—
Ce(IV)	9	—	—
Co(II)	9	−1·20	—
Co(III)	7	C.H.W.*	−0·60
Cr(III)	4	−1·14	−1·34†
Cu(II)	7	−0·32	−0·46†
Fe(III)	6	—	−0·48
Ga	6	—	—
In	9	—	−0·92
Mn(II)	10	—	—
Mn(III)	8	—	>0·0
Mo(VI)	2	−0·30 and −0·60	−0·82†
Nb(V)	4	—	—
Pb	8	ppte. at interface	
Pd	6	—	−0·74
Sc	7	—	—
Sn(II)	7	−0·78	—
Sn(IV)	7	—	—
Ti(III)	3	ppte. at interface	
Ti(IV)	3	−0·54	−0·80†
Tl(III)	7	—	—
U(VI)	4	−0·32, −0·69	—
V(V)	2	—	—
W(VI)	3	—	—
Zn	9	−1·08	—
Zr	2	ppte. at interface	

* C.H.W. denotes catalytic hydrogen wave.
† Extraction incomplete.

only between pH 6 and 9 for indium. The half-wave potential for palladium moved to more negative potentials with decreasing pH (from −0·70 to −0·78 V) and that for indium moved to more positive potentials (from −0·92 to −0·84 V).

A pH of 0·5 was chosen for further studies on palladium because no other ion is extracted at this pH,[8] and pH 9 was selected for determinations of indium to facilitate buffering of the solutions.

Solvents

These metals were also extracted by 0·1*M* solutions of acetylacetone in amyl acetate, isobutyl methyl ketone, chloroform and ethyl acetate. With neither metal (at the pH values chosen) did any of these solvents offer any advantages over toluene. Chloroform is itself reduced, with a wave at −1·0 V which tends to obscure the indium wave, and the other solvents produced maxima on the indium wave which could not be removed by the addition of cetyltrimethylammonium bromide or Methyl Red.

Acetylacetone concentration

The concentration of the ligand in toluene was varied over the range 1–500 × $10^{-3}M$. With both metals, the extraction was slow and incomplete, yielding elongated reduction waves, when the concentration of reagent was less than $10^{-2}M$. A slight shift in half-wave potential to more negative values was also observed with increasing ligand concentration. A concentration of 0·1*M* acetylacetone in toluene was chosen as being most suitable.

The effects of other parameters such as supporting electrolyte concentration and deoxygenation have been reported elsewhere.[5]

Procedure

Indium. Transfer by pipette 1–5 ml portions of indium solution (5 × $10^{-4}M$) into 100-ml separating funnels along with 2 ml of *ca.* $10^{-2}M$ aqueous acetylacetone, 5 ml of buffer solution (pH 9) and distilled water to give a volume of about 25 ml. Add 15 ml of the toluene reagent solution and shake for 1 min. Transfer the organic phase to a 25-ml standard flask containing 5 ml of 0·5*M* lithium chloride in methanol, and dilute to the mark with methanol. Deoxygenate a 5-ml portion of this solution for 5 min and record the polarogram. The height of the wave at −0·92 V *vs.* the mercury pool anode is proportional to the concentration of indium over the range 2–10 ppm (in the original solution). The relative standard deviation (9 results) for 4 × $10^{-5}M$ indium solution was 2·7%.

Palladium. The procedure is as for indium, except that the extraction is carried out at pH 0·5, obtained by the addition of concentrated hydrochloric acid and measured by pH-meter. The height of the wave at −0·78 V is proportional to the concentration of palladium over the range 2–10 ppm.

Extractions have also been made from up to 500 ml of aqueous solution containing the same amounts of the metals. Satisfactory results were obtained with the sensitivity thus increased to cover the range 0·1–0·5 ppm in the original solution.

Interferences

At pH 0·5 only palladium is extracted. The following elements, which are wholly or partially extracted by acetylacetone at higher pH, do not interfere in the determination of indium by this method: Al, Be, Ce(IV), Co(II), Cr(III), Cu(II), Fe(III), Ga, Mn(II), Mo(VI), Nb(V), Ni, Sc, Sn(II), Ti(IV), Tl(III), U(VI), V(V), Zn, and Zr. A 50-fold amount of palladium does not interfere in the determination of indium at the 5 × $10^{-5}M$ level.

Only Cu(II), Fe(III), Ti(IV) and Pd gave reduction waves in addition to indium, but the half-wave potential of the latter is sufficiently removed from the nearest of the others [Ti(IV) at −0·80 V] for there not to be any interference unless titanium is

present in very large amounts (the limit depending on the type of polarograph and its resolution). The waves of Cu(II), Ti(IV) and Pd may be eliminated by the addition of ascorbic acid and cyanide as masking agents, before the extraction. With warming, Fe(III) is also masked, though in the cold it is extracted as its acetylacetonate.

Reversibility

Plots of log $(i/i_d - i)$ *vs.* E made from the polarograms for solutions $4 \times 10^{-4}M$ in indium and palladium, were linear, with slopes giving values of n (the number of electrons in the electrode reaction) of 0·91 and 0·81 respectively. Conductivity measurements with a Philips PR9500 conductivity bridge and a normal conductivity cell showed that the solutions had a resistivity of 630 Ω-cm.

The determinations described are not the only ones that can be made using this particular system, although they are the most useful and easily applied. For example, the determinations of Cr(III) and Co(III) are also possible provided that the slow rate of formation of the complexes is accepted and, in consequence, the longer time required to carry out an analysis. The major advantage of the system is the ease with which a minor constituent may be separated, concentrated and determined, coupled with the short time required for the determination. Previously the determination of these metals was a lengthy and involved process in even relatively simple materials, *e.g.*, in the presence of Cd, Cu, Pb and Sn,[10] or in the presence of Cd, Cu, Pb and Zn.[11]

During the course of this study, benzoylacetone was also investigated as a possible extractant, and as an alternative to acetylacetone. However, the extraction of even copper and iron was very slow and it was considered that no advantage would be gained by its use.

Zusammenfassung—Indium und Palladium werden polarographisch mit einer Quecksilbertropfelektrode in Toluollösung bestimmt nach Extraktion der Acetylacetonate aus wäßrigen Lösungen, die 2–10 ppm der Metalle enthalten (oder 0,1–0,5 ppm mit einem größeren Verhältnis von Proben- zu Lösungsmittelvolumen). Unter 31 geprüften Elementen gaben nur Co(III), Cr(III), Cu(II), Fe(III), In, Mo(VI), Pd und Ti(IV) extrahierbare Komplexe mit Reduktionsstufen im zugänglichen Potentialbereich. Spezifität für Palladium erhält man durch Extraktion bei pH 0,5 und für Indium bei pH 9 in Gegenwart von Cyanid und Ascorbinsäure als Maskierungsmittel.

Résumé—On a dosé l'indium et le palladium par polarographie en phase toluénique avec une électrode à goutte de mercure après les avoir extraits, à l'état d'acétylacétonates, de solutions aqueuses contenant 2–10 p.p.m. des métaux (ou 0,1–0,5 p.p.m. avec un plus grand volume d'échantillon par rapport au volume de solvant). Des 31 éléments examinés, seuls Co(III), Cr(III), Cu(II), Fe(III), In, Mo(VI), Pd et Ti(IV) donnent des complexes extractibles avec des vagues de réduction dans le domaine de potentiel utilisable. On obtient la spécificité pour le palladium par extraction à pH 0,5 et pour l'indium à pH 9 en présence de cyanure et d'acide ascorbique comme agents de dissimulation.

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DETERMINATION OF URANIUM IN ELECTRO-REFINED PLUTONIUM BY A COMBINED ION-EXCHANGE AND X-RAY FLUORESCENCE TECHNIQUE*

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Summary—Uranium is separated from plutonium by adsorption on an anion-exchange resin from a concentrated hydrochloric acid solution and is eluted from the resin, collected on a disc of cation-exchange paper, and determined by X-ray fluorescence. The lower limit of detection is 2 μg of uranium, and 50 μg may be determined with a recovery of 98% and a standard deviation of 3·2 μg. In plutonium metal, 19 ppm of uranium were found, with a standard deviation of 2 ppm (6 results).

A METHOD was required for the determination of uranium as a trace impurity in electro-refined plutonium. The total impurity content in electro-refined plutonium is not expected to exceed 100 ppm. The techniques currently available for determining impurities in plutonium include optical emission spectroscopy, polarography, spark source mass spectrometry, and wet chemistry methods. Present optical emission and polarographic techniques lack the required sensitivity for the uranium determination. Plutonium-238 interferes with the uranium-238 determination by mass spectrometry. An ultraviolet fluorescence method for determining uranium, after separation from plutonium by fluoride precipitation, has been used successfully by our chemistry laboratory.

X-ray fluorescence techniques are generally not sensitive enough for trace analysis, and had not previously been considered for use in determining low-level impurities. Recent work reported by Spano, Green, and Campbell has shown, however, that X-ray fluorescence is capable of reaching the sensitivity needed.[1–3] They determined trace impurities in tungsten by adsorbing them on SA-2 cation–exchange paper, after preliminary separation from the tungsten matrix, and so concentrating the cations in a matrix that permits quantitative detection of microgram amounts of them by X-ray fluorescence. It seemed reasonable to suppose that this approach could be used for determining trace level uranium in plutonium.

EXPERIMENTAL

Apparatus

Ion-exchange separations were made on small polyethylene columns, 0·5 in. diameter and 3 in. long, containing 2 ml of the resin. The uranium was concentrated by filtering the solution through a 1-in. diameter disc of SA-2 paper. The filtering device shown in Fig. 1 is simple to prepare and can be discarded after use. A polyethylene bottle with a 1-in. o.d. screw cap is cut in two sections. A $\frac{7}{8}$-in. hole is cut in the cap, and the resin disc is placed inside the cap. The cap is screwed on the bottle, and the inverted bottle top is placed on the severed bottom. The solution is poured into the inverted top, caught in the severed bottom and returned to the beaker for refiltering.

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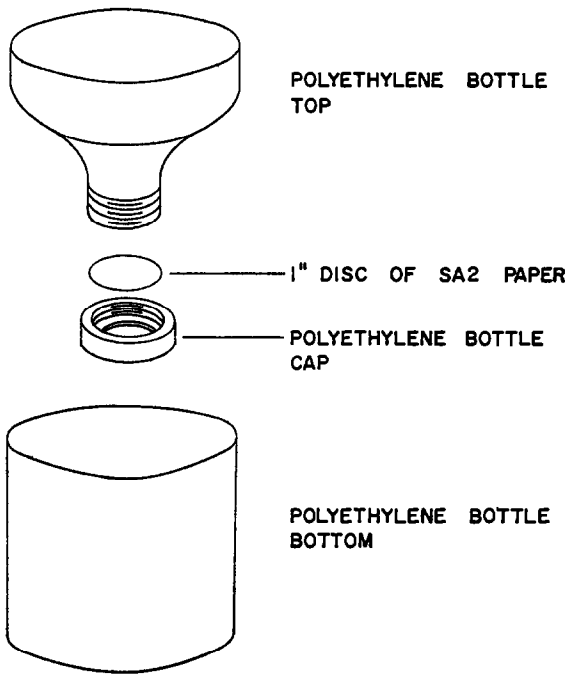

FIG. 1.—Disposable filtering device.

The loaded disc was mounted on a 1-in. i.d. pipe cap covered with 0·25 ml Mylar film and dried under an infrared lamp.

A Phillips–Norelco 100 kV constant-potential X-ray spectrograph was used to analyse the disc for its uranium content.

Reagents

Solution A. Concentrated hydrochloric acid containing 0·01 mole of ascorbic acid per l.

Solution B. A solution of pH 2 was prepared by mixing 1 ml of conc. hydrochloric acid with 1 l. of water. The pH was checked with narrow-range indicator paper.

Methanol, dried.

All reagents were chemically pure materials.

Ion-exchange resins

Anion-exchange resin. Dowex 1-X4, 100–200 mesh, was conditioned by washing with 10 column-volumes each of water, methanol, and solution A.

Cation-exchange resin. Dowex 50-X4, 100–200 mesh, was conditioned by washing with 10 column-volumes each of 3*M* hydrochloric acid, conc. hydrochloric acid, water, and solution B.

SA-2 paper (Reeve Angel Corporation, Clifton, New Jersey) is impregnated with Amberlite IR-120 cation-exchange resin in the sodium form. One-inch discs were cut from the sheets and conditioned with 20 ml each of 3*M* hydrochloric acid and water, returned to the sodium form by soaking in saturated sodium chloride solution, and finally rinsed with several ml of solution B.

Procedure

Dissolve a 1-g sample in 5 ml of conc. hydrochloric acid to which 10 mg of ascorbic acid have been added to keep plutonium in the tervalent state. Add a few drops of water to prevent precipitation of $PuCl_3$ if larger samples are dissolved. Pass the solution through the anion-exchange column. The resin adsorbs the uranium quantitatively while retaining only about 1 mg of plutonium. Wash the column with 20 ml of solution A to rinse the beaker and flush plutonium through the resin, and then with 20 ml of dry methanol. Elute the adsorbed ions with 20 ml of solution B. Pass the eluate through the cation-exchange column; both uranium and plutonium are adsorbed. Elute the cations from the column with 20 ml of solution A.

Pass this eluate through another column containing fresh Dowex 1 × 4, and use several ml of solution A to rinse the beaker and transfer the solution completely. Uranium is adsorbed and plutonium is not. Wash the resin with 20 ml of dry methanol, and again elute with 20 ml of solution B. Pass this eluate through an SA-2 cation-exchange paper disc five times to ensure complete adsorption of the uranium; the flow-rate is about 10 ml/min. Pass the eluate five times through a second disc to check that recovery is complete.

Mount the wet discs on the Mylar-covered plastic pipe caps, with the surface first contacted by the solution face down on the Mylar. Dry the discs with low heat from an infrared lamp, cover them with two layers of Mylar film, and seal with a curtain ring and tape. Check the outside surface of the Mylar film, the curtain ring and the tape for contamination before removal from the hood. Put the mounted disc in the sample chamber of the X-ray unit for analysis.

Instrument parameters are as follows:

1. Tube	Tungsten
2. Power	50 kV, 33 mA
3. Crystal	LiF
4. Detector	Scintillation, 875 V
5. PHA	Base Line 10·5 V, Window 16 V
6. Goniometer	26·14° $U_{L\alpha 1}$ 27·50° Background

Prepare a standard curve by carrying a set of standard solutions through the procedure. Plot intensity ratios (I_U/I_{bg}) *vs.* concentration on linear graph paper for the 0–300 μg range. At higher concentration ranges (1000–4000 μg) use semi-log paper. The intermediate range should be avoided for reasons that will be discussed later.

DISCUSSION

The strongest uranium line that can be excited with the 100 kV spectrograph is the first-order $L_{\alpha 1}$ line at $2\theta = 26{\cdot}14°$. The first-order plutonium $L_{\alpha 1}$ line falls at $2\theta = 24{\cdot}92°$. Since both lines are first-order, pulse height discrimination cannot be used to eliminate interference from plutonium. Prior removal of gross amounts of plutonium is necessary if microgram quantities of uranium are to be detected. Plutonium(III) can be separated from uranium(IV) by adsorption of the uranium on an ion-exchanger.

Ascorbic acid was used as the reducing agent because it effectively reduces plutonium to the tervalent state and keeps it there without introducing foreign cations into the system. The concentration of ascorbic acid was varied from 0·01 to 0·2*M* without adversely affecting the analysis. Since plutonium(III) is formed in the dissolution step, the ascorbic acid is needed primarily to prevent auto-oxidation. A 0·01*M* concentration of it was adequate.

After the uranium is loaded on the anion–exchange column the concentrated acid must be removed; this can be done with methanol. Uranium can then be eluted from the anion column and loaded onto the cation–exchange resin with a solution at pH 2. Figure 2 shows the elution curve from Dowex 1 × 4 with this element. Other techniques for eliminating the concentrated acid were investigated. Evaporation after elution of the uranium from the column was both time-consuming and inconvenient. Neutralizing the acid with dis-iopropylamine was tried in the hope that the cation formed would be too large to compete with uranium for exchange sites on the resin, so making use of the principle of ion-exclusion. Unfortunately, it did compete and the uranium exchange capacity was reduced. Washing the acid from the column with acetone was not efficient and created problems with bubble formation in the column. The best method was the methanol wash which effectively removed the acid from the column without eluting uranium or interfering with subsequent steps.

The extent of separation that can be achieved is shown in Table I. A separation factor of $10^{2{\cdot}5}$ can be obtained on the first pass through the Dowex 1 column and a separation factor of 10^5 when a double separation is used.

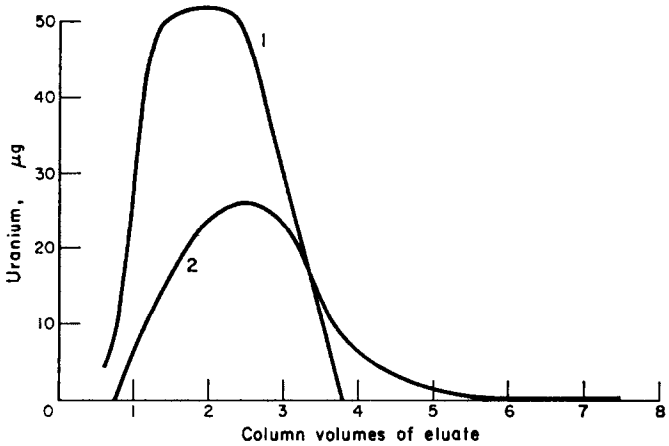

FIG. 2.—Elution curves.
1. Uranium from Dowex 1 with eluent at pH 2.
2. Uranium from Dowex 50 with conc. HCl.

TABLE I.—SEPARATION OF PLUTONIUM FROM URANIUM BY ANION-EXCHANGE IN A CHLORIDE SYSTEM

Single separation		Double separation	
Pu added, μg	Pu not separated, μg	Pu added, μg	Pu not separated, μg
$9{\cdot}45 \times 10^5$	6×10^2	$9{\cdot}39 \times 10^5$	10
$9{\cdot}51 \times 10^5$	5×10^2	$9{\cdot}45 \times 10^5$	5
$9{\cdot}33 \times 10^5$	7×10^2	$9{\cdot}61 \times 10^5$	5
$9{\cdot}56 \times 10^5$	7×10^2	$9{\cdot}96 \times 10^5$	10
$9{\cdot}76 \times 10^5$	5×10^2	$3{\cdot}96 \times 10^5$	10

For the double separation the two cations eluted from the first Dowex 1 column can be loaded on the second Dowex 1 column by evaporating the solution to incipient dryness and taking up the cations in conc. hydrochloric acid, or by loading the cations on Dowex 50 resin and eluting them with the desired volume of conc. hydrochloric acid.

The second method was selected, since the first is time-consuming and inconvenient. Figure 2 also shows the elution curve for uranium from Dowex 50 with 11·7*M* hydrochloric acid.

Ion-exchange paper

After double separation the plutonium remaining in solution (about 10 μg) is well below a level that would interfere (>300 μg), and the uranium can then be concentrated on the cation-exchange disc. The disc is the size of the X-ray beam striking the sample, weighs about 55 mg and consists of about 50% paper–50% IR 120 cation-exchange resin (Na^+).

The theoretical capacity of SA-2 paper is about 2 m-equiv/g.[1] A 1-in. disc of the paper (55 mg) should have a theoretical capacity of 0·11 m-equiv. or about 6,000 μg of

uranium(IV). The working capacity of the resin discs was established by filtering a solution containing up to 6000 μg of uranium five times through an SA-2 disc and then fives times through a fresh disc. The uranium contained on the second disc indicated the amount not adsorbed by the first.

Under the conditions used, the maximum working capacity of the 1-in. disc was about 4000 μg.

The pH of the loading solution was selected on the basis of Campbell's report[1] which indicates that below pH 1 hydrogen ion competes to some extent with metal ions

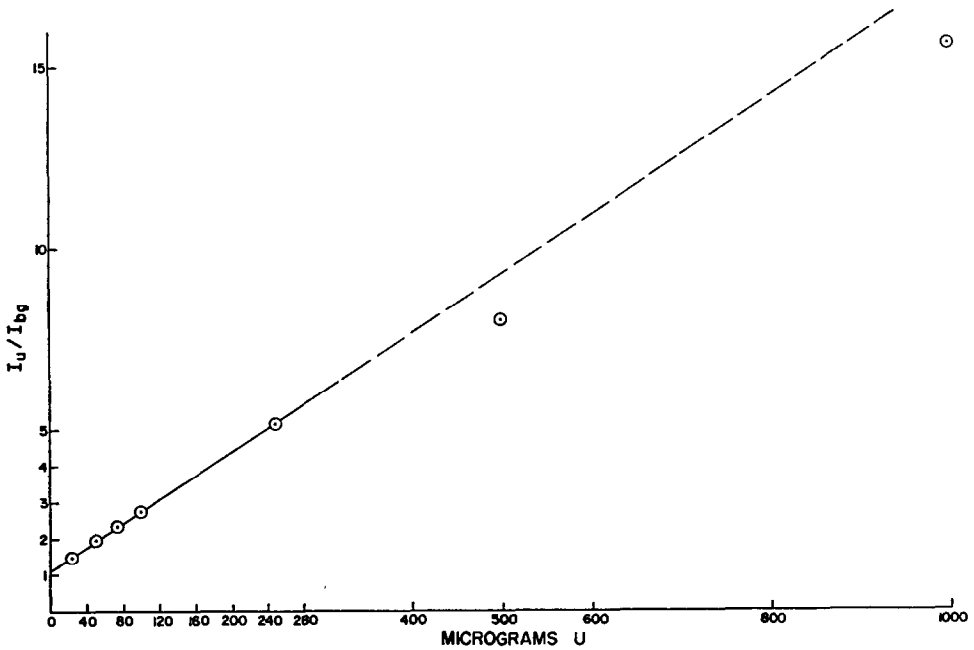

FIG. 3.—I_U/I_{bg} *vs.* amount of U—linear plot.

for available exchange sites whereas above pH 3 some metal ions tend to precipitate. He encountered no difficulty with solutions at pH 2.

Campbell[1] reported that 80% of the cation present (Co) was adsorbed during the first filtration, and quantitative adsorption was accomplished in 3–5 filtrations. Similar behaviour occurred with 100 μg of uranium, about 80% of the amount present being adsorbed at each pass; when 2000 μg of uranium were used, 96% was recovered on the first disc in five passes.

Papers were dried under low heat from an infrared lamp. Oven drying involved more handling, and the disc had a tendency to curl around the edge. Acetone will dry the disc by removing water without eluting uranium, but does not always completely remove the moisture.

The relationship between the amount of uranium on the paper and the intensity ratio (I_U/I_{bg}) varies, depending on the concentration. The relationship is directly proportional from 0–300 μg of uranium and for larger amounts is non-linear due to self-absorption of the uranium radiation (Figs. 3 and 4).

All results in this report were obtained by analysis of one side (bottom) of the disc. Uranium radiation is relatively hard and not significantly absorbed by the paper.

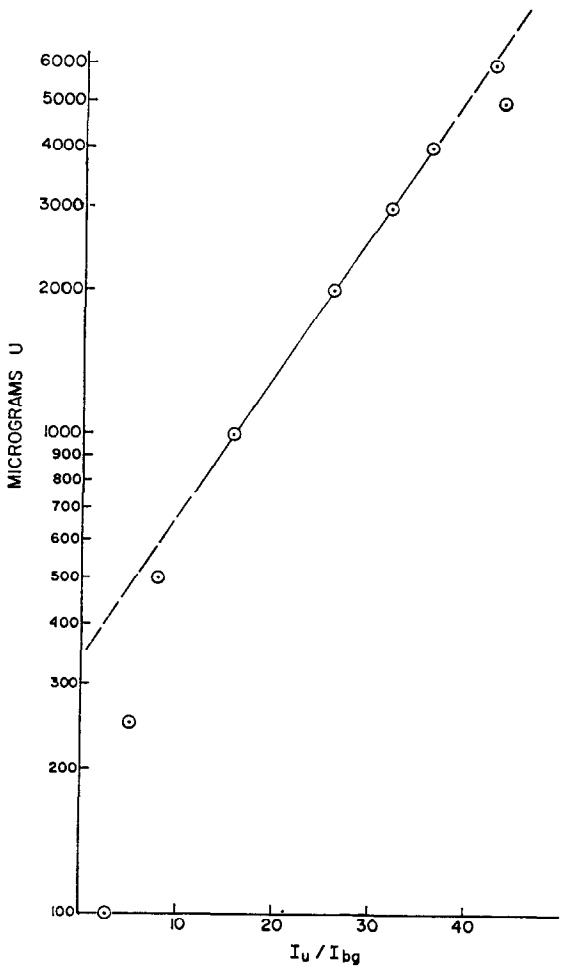

FIG. 4.—I_U/I_{bg} *vs.* amount of U—semi-logarithmic plot.

When both sides of a disc loaded with 50 μg of uranium were analysed no difference in the intensity of uranium radiation could be detected; however, for the soft radiation coming from low-atomic-number elements, absorption by the paper would be significant and placement of the disc for analysis would become a factor.

Interferences

The method is designed for ultra-pure plutonium. In such material the total content of impurities is not expected to exceed a few hundred ppm. Low concentrations of cations that might be present will not interfere with the uranium analysis. For less pure material the effect of other cations must be considered. The disposition of other cations present at the beginning of the analysis would be as follows.

The alkali metals, alkaline earths, rare earths, aluminium, nickel, yttrium and thorium are separated from uranium along with the plutonium. These thirty elements were not tested; however their adsorption characteristics on Dowex 1 X4 resin from conc. hydrochloric acid have been established by other workers.[4]

Chromium, iron, cobalt, copper, and zinc were tested qualitatively. They accompany uranium to varying degrees. If present in large amounts, they would interfere by using up exchange sites on both the anion- and cation-exchange resins. The degree of interference would have to be determined for specific concentrations.

Gallium and iron were tested, and found to be adsorbed by Dowex 1 and Dowex 50; however, they are not eluted from the cation-exchange resin with conc. hydrochloric acid. Though they do not follow uranium through the analysis, large amounts will interfere by competing with uranium for exchange sites on the resin columns. Gold was not tested but would be expected to interfere in the same manner as gallium and iron.[4,6]

Zirconium, hafnium, and neptunium were not tested, but their distribution coefficients, measured by Kraus and Nelson,[4] indicate that they would accompany uranium. Absorption of characteristic uranium radiation by these elements must be considered if the total cation content on the disc exceeds 0·005 m-equiv. (300 μg of uranium).

Three common anions, sulphate, nitrate, and fluoride, were tested to determine their effect on the analysis. In conc. hydrochloric acid, small amounts of sulphate (<0·15 m-equiv/ml) have no effect on the retention of uranium by the anion-exchange resin. The uranium solution to be passed through the SA-2 paper can be adjusted to pH 2 with sulphuric acid without hindering the uranium adsorption. Recovery of 50 μg of uranium was complete when the acidity was adjusted from pH 7 to pH 2 with sulphuric acid.

Small amounts of nitrate in conc. hydrochloric acid hinder the uranium–plutonium separation on the anion-exchanger by oxidizing plutonium(III) to the plutonium(IV). Additional ascorbic acid must be used to counteract oxidation by nitrate. Uranium (50 μg) was completely adsorbed by SA-2 paper from nitric acid solution at pH2.

Small amounts of fluoride (<0·15 m-equiv/ml) in conc. hydrochloric acid have no effect on the anion-exchange adsorption of uranium, but fluoride drastically interferes with the sorption of uranium by the cation-exchanger from pH 2 solutions. The uranium loss from the SA-2 paper was 75% when the pH was adjusted from 7 to 2 with hydrofluoric acid.

RESULTS

Six solutions, each containing 50 μg of uranium only, were carried through the entire procedure and the discs counted twice at each goniometer setting. The average values were used to calculate the amount of uranium present. The results are summarized in Table II. Precision data were obtained from six samples cut from a piece of

TABLE II.—SOLUTIONS CONTAINING 50 μg U ONLY

Sample	U recovered, μg
1	49·7
2	49·5
3	47·2
4	54·7
5	45·7
6	47·0
Mean recovery	48·9 μg (98%)
Standard deviation	3·2 μg
Relative standard deviation	6·5%

electro-refined plutonium. The results are listed in Table III. Accuracy data were acquired on five pieces cut from an electro-refined metal sample, which were spiked with varying amounts of uranium. The results are listed in Table IV. The minimum detectable amount, taken as three times the standard deviation of a blank sample, was 1–2 μg of uranium. The upper limit was 300 μg. Above this level self-absorption effects must be taken into account and higher uranium concentrations might best be determined by another procedure.

TABLE III.—PRECISION

Sample, g	U found	
	μg	ppm
0·5075	8·5	16·7
0·9429	16·0	17·0
0·9997	19·0	19·0
2·4619	49·0	19·9
0·9692	19·5	20·1
3·8875	86·0	22·1
	Mean	19·1 ppm
	Standard deviation	2·0 ppm
	Relative standard deviation	10%

TABLE IV.—ACCURACY

Sample, g	U present, μg	U added, μg	U found, μg	Recovery, %
0·9468	unknown	0	2·5	–
0·3955	1·0	5·0	6·0	100
0·9605	2·5	25·0	28·0	102
0·9955	2·5	30·0	32·0	98
0·9391	2·5	50·0	60·5	116
0·0	0	100·0	97·0	97
			Mean recovery	103%
			Standard deviation	8%

OTHER APPLICATIONS

The procedure could probably be used for the determination of zirconium and hafnium in plutonium. Plutonium(IV) forms an anionic nitrate complex which can be separated from elements that do not form nitrate complexes[7] by adsorbing it on an anion-exchange resin from 8*M* nitric acid. The separated elements could then be concentrated on SA-2 paper after removal of the nitric acid. The nitrate separation procedure is currently used at several AEC laboratories in conjunction with optical emission spectroscopy for determining common impurities. It could conveniently be adapted for use with ion–exchange paper and X-ray fluorescence techniques. An attempt to use the papers in infrared and ultraviolet analysis was unsuccessful.

Preliminary tests with neptunium indicated that the papers could be used in conjunction with radiochemical analysis. Gamma-emitting isotopes can be concentrated on the paper and determined with a scintillation detector. Experiments with SB-2 anion–exchange papers in conc. hydrochloric acid were moderately successful in that adsorption of the neptunium anionic chloride complex was directly proportional to the concentration of neptunium in the solution. It was not, however, quantitative.

CONCLUSION

The determination of trace amounts of uranium by X-ray fluorescence can be accomplished with good precision and accuracy. The sensitivity of X-ray fluorescence as an analytical tool is effectively extended by the technique of concentrating trace impurities on ion–exchange paper.

Acknowledgement—The author would like to thank Dr. W. J. Campbell and his coworkers at the Bureau of Mines, College Park, Maryland, for sending reports on their work with ion-exchange paper. These reports were a valuable aid in the development of this method.

Zusammenfassung—Uran wird von Plutonium getrennt durch Adsorption aus konzentriert salzsaurer Lösung an einem Anionenaustauscher und wird vom Harz eluiert, auf einer Scheibe Kationenaustauscherpapier gesammelt und durch Röntgenfluoreszenz bestimmt. Die untere Nach-weisgrenze ist 2 μg Uran; 50 μg können mit einer Ausbeute von 98% und einer Standardabweichung von 3,2 μg bestimmt werden. In metallischem Plutonium wurden 19 ppm Uran gefunden mit einer Standardabweichung von 2 ppm (6 Ergebnisse).

Résumé—L'uranium est séparé du plutonium par absorption sur une résine échangeuse d'anions à partir d'une solution en acide chlorhydrique concentré puis élué de la résine, recueilli sur une rondelle de papier échangeur de cations et dosé par fluorescence aux rayons X. La limite inférieure de détection est de 2 μg d'uranium et l'on peut doser 50 μg avec une récupération de 98% et un écart type de 3,2 μg. Dans le plutonium métallique, on a trouvé 19 p.p.m. d'uranium avec un écart type de 2 p.p.m. (6 résultats).

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SPECTROPHOTOMETRIC EXTRACTIVE TITRATIONS—IV*
DETERMINATION OF ZINC IN GERMANIUM DIOXIDE AND GERMANIUM CHLORIDE

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Summary—A simple and selective determination of zinc in germanium chloride and germanium dioxide is described. The sample is dissolved in sodium potassium tartrate solution and zinc is titrated spectrophotometrically at 532 mμ with a dithizone solution in carbon tetrachloride without discarding the organic phase. Interfering ions such as Bi(III), Cu(II), Cd(II), Co(II), Ni(II), Pb(II), Sn(II), Fe(II), Fe(III), Mn(II) and Tl(I) are masked with bis(2-hydroxyethyl)dithiocarbamate. The detection limit is $3{\cdot}23 \times 10^{-5}$% of zinc and this may be lowered by taking a larger sample and by performing the analysis in a closed system. A simplified technique, consisting of the simultaneous titration of the sample and blank, is described.

IN PART III[1] the determination of silver and copper with dithizone was described. The procedure was selective because the dithizonates of these elements have extraction constants much higher than those of most other dithizonates. The present paper deals with the spectrophotometric extractive titration when the extraction constant is much less favourable *viz.*, zinc with dithizone. The conditions—pH, masking agent, wavelength, *etc.*—must be chosen so that the elements which form more stable dithizonates are not titrated at all and those that form less extractable dithizonates are titrated only partially, if at all.

It is preferable if these conditions allow the application of the procedure to the determination of zinc in germanium dioxide and germanium chloride without the separation of the matrix, because the separation procedures generally used may lead to contamination of the sample or to loss of zinc.

The dissolution of samples in sodium potassium tartrate solution was chosen because tartrate ion successfully prevents the precipitation of germanium dioxide but does not significantly affect the extraction of zinc with dithizone. Another advantage is the possibility of purifying the tartrate solution with dithizone, thus lowering the value of the blank. The limiting circumstance is that only hexagonal GeO_2 can be dissolved in this way. The use of tartrate medium determines the pH range for titration as 8–9.[2]

Bis(2-hydroxyethyl)dithiocarbamate (diethanoldithiocarbamate) was chosen as a masking agent for other metal ions which would react with dithizone. It has been used, in conjunction with cupferron to remove iron and copper, to make the determination of zinc with the dithizone single colour method very selective.[3] This method, modified by the use of sodium sulphide for stripping the excess of dithizone, was found to be the most selective of seven methods of zinc determination.[4] Thus, though it might seem that the application of spectrophotometric extractive titration

* Part III—*Talanta*, 1966, **13**, 1169.

to this determination is pointless, this technique may simplify the whole procedure, because stripping of excess of dithizone is not necessary and consequently a lower contamination hazard may be expected.

EXPERIMENTAL

The apparatus and common reagent solutions have been described previously[1,2,5]; only solutions and modifications not described earlier are listed below.

Apparatus

Titration assembly. Titrations were performed in titration cells similar to those described earlier,[5] but with the cell holder adapted for the Zeiss Universalspektrophotometer VSU—1 (Zeiss, Jena), which was used for measurement of the absorbance.

Reagents

Sodium potassium tartrate solution, 20% w/v. Purify with dithizone as described earlier.[2]

Masking solution. Add dropwise 3·5 g of carbon disulphide to 6 g of diethanolamine in 120 ml of methanol, keeping the solution cool, and dilute to 200 ml with water. Purify this solution in the same manner as the tartrate solution.

Hydrochloric acid, transistor grade.

Dithizone, 10^{-4} *to* 5×10^{-5} *M*. The solution in twice-distilled carbon tetrachloride was purified as required.[6]

Standard zinc solution. Dissolve 0·100 g of zinc in hydrochloric acid, dilute to 1 l. and then dilute this solution 50-fold immediately before use. Keep the dithizone solution in a quartz bottle, and all other solutions in polyethylene bottles.

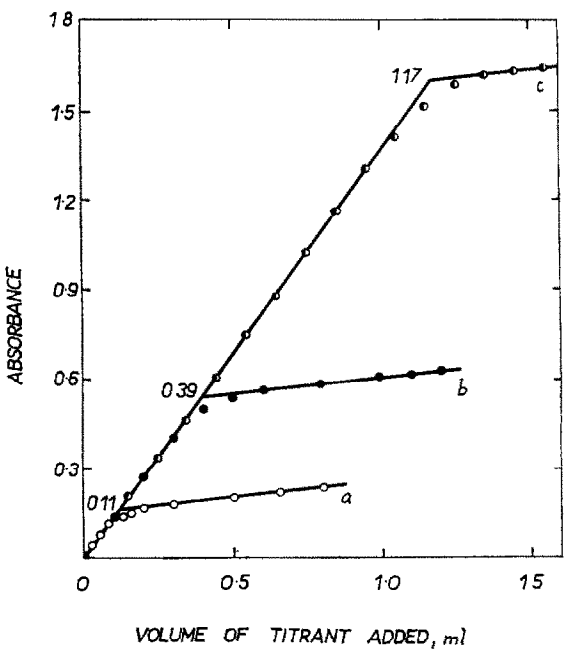

FIG. 1.—Titration of zinc with $10^{-4}M$ dithizone in CCl_4.
Curve *a*—blank titration.
Curve *b*—titration of 2-g sample of GeO_2.
Curve *c*—titration same sample as for *b*, but with 2·50 μg Zn added.

Procedure

Analysis of samples. Dissolve 2 g of the germanium dioxide or tetrachloride sample in 50 ml of sodium potassium tartrate solution in a 100-ml quartz beaker. Add 3·00 ml of the masking solution and adjust to pH 8–9 (pH paper) with few drops of ammonia solution or hydrochloric acid added from a polyethylene pipette. Transfer the solution into one of the titration cells containing 5–10 ml of

carbon tetrachloride. Titrate extractively with dithizone, using a microburette. Shake for 2 min after each addition of titrant and measure the absorbance at 532 mμ against carbon tetrachloride shaken with 50 ml of tartrate solution. Plot the absorbance *vs.* volume of dithizone added, so obtaining the titration curve. The shape of the curve is similar to that for titration of cadmium, see Part I[5] and Fig. 1. Note the consumption of dithizone, *a* ml.

Blank. Carry out the same procedure without the sample. Note the consumption of dithizone, *b* ml.

Standardization. Add 2·00 ml of standard zinc solution (4·00 μg of zinc) to 50 ml of tartrate solution in a 100-ml quartz beaker and mix for the time taken to dissolve the samples. Add 3·00 ml of the masking solution and titrate as described above. The volume of dithizone found, *c* ml, corresponds to the sum of the zinc added and the blank.

Calculation of results. The zinc content, *X*, in the sample is given by the relation:

$$X = \frac{(a-b)}{(c-b)} \cdot \frac{4 \times 10^{-4}}{\text{Sample weight}} \%,$$

where the sample weight is expressed in g.

RESULTS AND DISCUSSION

Selectivity

Because the stripping of excess of dithizone, a step used by Margerum and Santacana,[4] was omitted, it was necessary to check the selectivity. Solutions of sodium potassium tartrate containing known amounts of zinc and other metals were titrated in the presence of diethanoldithiocarbamate as described above. The results were compared with those obtained for pure solutions of zinc. From the results shown in Table I it may be concluded that the titration of zinc by this procedure is highly selective; bismuth, copper, cobalt, nickel, cadmium, lead, iron(II), and (III), manganese, thallium and tin(II) do not interfere. Other metals such as mercury and silver which form dithizonates would not be expected to interfere.[7] Indium is not extracted to any significant extent over the pH range used.[2]

TABLE I.—SELECTIVITY OF THE TITRATION OF ZINC

Zinc present, μg	Zinc found, μg	Difference, %	Other metals present, μg
3·58	3·66	+2·2	2·57 Cu
3·58	3·64	+1·7	45 Cu
3·58	3·55	−0·8	90 Cu
3·58	3·58	0	100 Cd
3·58	3·78	+5·6	200 Ni, 200 Pb and 100 Bi
3·58	3·42	−4·5	200 Co, 200 Cd and 90 Cu
7·16	7·80	+9	200 Mn, 200 Ni
7·16	7·40	+3·4	200 Tl, 200 Bi
7·16	6·56	−8·4	200 Mn, 200 Tl and 200 Sn
7·16	6·80	−5	200 Fe(II) and 200 Ni
7·16	7·60	+6·2	90 Cu, 200 Fe(III)

The selectivity was compared with that of the single colour zinc determination by extraction with an excess of dithizone at pH 8–9. Instead of sodium sulphide, dilute aqueous ammonia was used as stripping agent. Serious interference from copper and cadmium was observed, emphasizing the advantages of the titration procedure.

TABLE II.—RECOVERY OF STANDARD ADDITIONS

Sample	Zinc added, μg	Zinc recovered*	
		μg	%
GeO_2	2·50	2·70	107
GeO_2	2·50	2·38	95
GeO_2	2·50	2·38	95
GeO_2	3·00	3·15	105
GeO_2	3·00	2·70	90
GeO_2	3·00	3·00	100
GeO_2	7·16	7·71	108
GeO_2	7·16	6·93	97
$GeCl_4$	3·00	2·94	98
$GeCl_4$	7·16	7·63	105
$GeCl_4$	8·92	8·70	97

* Blank value and sample content subtracted.

Recovery of standard additions

Because of the lack of germanium dioxide or germanium chloride with a known zinc content the proposed titration procedure was checked by standard additions to samples of which the zinc content was determined by this procedure. The standard additions were made to analysed samples before their dissolution. Results of these experiments given in Table II show the precision of the method.

Sensitivity

During the analyses involving standard additions, blank values were obtained. The standard deviation of the blank was found from 20 results to be 0·305 μg of zinc. Consequently, the detection limit is 0·7 μg of zinc, *i.e.*, 3×10^{-5}% of zinc for a triplicate analysis of a 2 g sample and triplicate blank determinations. This high value is probably due to all the experiments being performed in a technological laboratory under conditions where it was not possible to apply the enclosed system[8] and so keep the blank value low. It is possible to lower the detection limit by increasing the sample weight, and this is especially easy in the case of germanium chloride.

Simultaneous titration of the blank and sample

The titration described takes about 30 min (if 5 points on each branch of the titration curve are necessary to establish the end-point. Because titration of the blank takes about the same time, an attempt was made to titrate sample and blank simultaneously.

Procedure. Dissolve 2 g of the sample in 50 ml of sodium potassium tartarte solution in a 100-ml quartz beaker, add 3·00 ml of masking solution and adjust the pH of the solution to 8–9. Prepare the blank by mixing the same volumes of reagents for the same length of time. Transfer both solutions into titration cells and add to them the same volumes of carbon tetrachloride (5 to 10 ml according to the zinc content expected). Titrate with dithizone solution by adding precisely the same volumes of titrant to both cells. After each addition shake for 2 min and, when the organic phases have become clear, measure the absorbance of the sample against the blank, at 532 mμ. The absorbance does not change very much until the zinc in the blank is incompletely extracted. Then the absorbance increases, as the zinc in the sample is titrated until the end-point is reached, The titration volume is the volume between the first and the second breaks of the titration curve, typified by Fig. 2.

The simultaneous titration of sample and blank takes only 45 min, compared to 1 hr when the titrations are performed separately, and results in a lower contamination hazard and eliminates most of the error connected with changes of contamination hazard during the analysis.

There are also other advantages of the simultaneous titration technique. When germanium dioxide is to be analysed, the dissolution of the sample is performed simply by mixing the sample with sodium potassium tartrate solution at a pH previously adjusted to 8–9. During the dissolution essentially no change of pH occurs, so it is evident that the pH of the blank and sample solutions are the same, and hence there is the same distribution of free dithizone between the aqueous and organic phases in both cells. Because only the difference in absorbance is measured, the slope of the titration curve after the end-point must be zero.

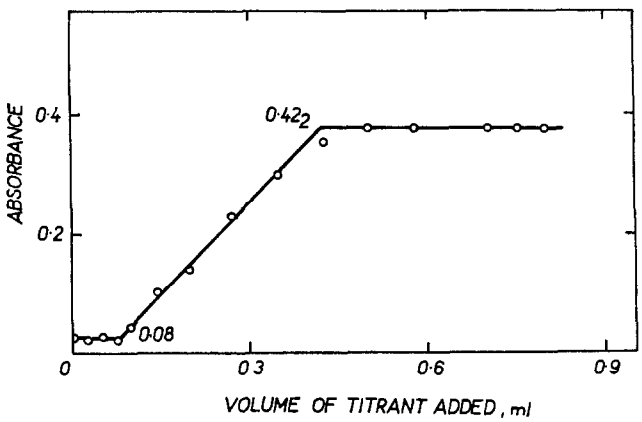

FIG. 2.—Simultaneous titration of zinc in GeO_2.

In the analysis of germanium tetrachloride, neutralization of the hydrochloric acid liberated during dissolution is necessary. Thus neither the same pH nor the same distribution of free dithizone in both cells is to be expected. When the sample and blank are titrated independently, the equation of the titration curve sufficiently far after the end point may be written as follows:

$$A = k \cdot \frac{m_{H_2Dz}}{V_{org}} \cdot \frac{1}{\left\{1 + \frac{V_{H_2O}}{V_{org}} \cdot \frac{K_{HA}}{q[H]}\right\}} + A_{Zn(HDz)_2}$$

where k is the product of the length of the light-path and the molar absorptivity of dithizone at 532 mμ, m_{H_2Dz} is the number of moles of excess of dithizone added after the end-point, V_{H_2O} and V_{org} are the volumes of the aqueous and organic phases respectively, K_{HA} (2×10^{-5}) is the acid dissociation constant of dithizone,[9] q($1{\cdot}1 \times 10^4$) is the distribution coefficient of dithizone between water and carbon tetrachloride,[9] $A_{Zn(HDz)_2}$ is the absorbance of the zinc dithizonate, and [H] is the concentration of hydrogen ions in the aqueous phase. As the pH of the solution may vary from 8 to 9 in the procedures described, the slope of the titration curve after the end-point may

vary from about 0·5 k/V_{org} for pH 8 to about 0·1 k/V_{org} for pH 9. If simultaneous titration is used, the slope of the titration curve after the end-point may vary over the range $\pm 0{\cdot}4\ k/V_{org}$, and if it is $<0{\cdot}1$ simultaneous titration gives better location of the end-point. The saving of time, however, may lead to preference of simultaneous titration even for zinc in germanium tetrachloride. Simultaneous titration may fail if the zinc content is so low that no distinct break appears on the curve after the blank has been titrated.

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Zusammenfassung—Ein einfaches und selektives Verfahren zur Bestimmung von Zink in Germaniumchlorid und Germaniumdioxid wird beschrieben. Die Probe wird in Natriumkalium tartratlösung gelöst und Zink spektrophotometrischen bei 532 nm mit einer Dithizonlösung in Tetrachlorkohlenstoff titriert, ohne daß die organische Phase abgetrennt wird. Störende Ionen wie Bi(III), Cu(II), Cd(II), Ni(II), Pb(II), Sn(II), Fe(II), Fe(III), Mn(II) und Tl(I) werden mit Bis(2-hydroxyäthyl)dithiocarbamat maskiert. Die Nachweisgrenze ist $3{,}23.10^{-5}$% Zink; sie kann gesenkt werden durch Verwendung einer großeren Probe und Ausführen der Analyse in einem geschlossenen System. Es wird auch ein vereinfachtes Verfahren beschrieben, das in der gleichzeitigen Titration von Probe und Blindprobe besteht.

Résumé—On décrit une méthode simple et sélective pour le dosage du zinc dans le chlorure et le bioxyde de germanium. On dissout l'échantillon dans une solution de tartrate de sodium et potassium, et titre le zinc par spectrophotométrie à 532 mμ avec une solution de dithizone dans le tétrachlorure de carbone sans séparation de la phase organique. Les ions gênants comme Bi(III), Cu(II), Cd(II), Co(II), Ni(II), Pb(II), Sn(II), Fe(II), Fe(III), Mn(II) et Tl(I) sont dissimulés par le dithiocarbamate de bis(2-hydroxyéthyle). La limite de détection est de $3{,}23 \times 10^{-5}$% de zinc et peut être abaissée en prélevant un échantillon plus important et en menant l'analyse dans un système clos. On décrit une technique simplifiée, consistant à titrer simultanément l'échantillon et le témoin.

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FORMATION OF MIXED COMPLEXES IN THE EXTRACTION OF INDIUM WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL

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Summary—A detailed study has been made of the extraction of indium into chloroform by 1-(2-pyridylazo)-2-naphthol (PAN). The rate of extraction is maximal if the PAN is added to the aqueous phase and is not added as its chloroform solution. The ratio of indium to PAN is 1:1 and the cationic complex can be extracted only if a suitable anion is present, such as acetate or chloride.

INDIUM forms a brightly coloured chelate compound with 1-(2-pyridylazo)-2-naphthol, and this compound may be extracted into chloroform and other solvents.[1,2] The conditions of formation of this compound and its spectrophotometric uses have been studied.[3–5] The compound was extracted from an acetate buffer, and an ethanolic or methanolic solution of PAN was added to the aqueous phase, the phases then being shaken for several minutes. The extraction mechanism of PAN complexes of indium and other metals has been insufficiently studied. According to the literature[3–9] indium and some other multicharged cations react with PAN in the ratio 1:2 or 1:1. Cheng and Goydish, however, assign the composition $In_2(PAN)_3$ on the basis of spectrophotometric molar ratio studies.[10] In a 1:1 or a 1:2 ratio however, PAN (a monobasic acid) would not be able to form a neutral complex with indium. In that case the complex would only be extractable into chloroform if a suitable anion formed a neutral ternary complex with it. This problem was investigated in the work described here.

EXPERIMENTAL

Reagents

Indium nitrate solutions were prepared, $2{\cdot}0 \times 10^{-3}$ and $3{\cdot}1 \times 10^{-4}M$, tagged with ^{114m}In and containing nitric acid (0·06*M*).

PAN solutions in chloroform or ethanol were accurately prepared from the solid reagent (Reanal, Hungary) the purity of which was checked by spectrophotometric titration with copper.[11]

Chloroform was purified by washing with small amounts of water, and distillation after drying over calcium chloride: 1% v/v of ethanol was added as stabilizer.

Buffer solutions included 0·2*M* sodium acetate adjusted to pH 5·9–7·0 with acetic acid or to pH < 5·3 with hydrochloric acid; hexamine at pH 6·1 (28·5 ml of 1*M* hexamine and 7·0 ml of 1*M* hydrochloric acid mixed and diluted to 100 ml); 0·2*M* potassium hydrogen phthalate and 0·05*M* citrate.[12]

Solutions of lithium chloride, sodium perchlorate and sodium nitrate were made from chemically pure reagents.

Procedure

The extractions were carried out in graduated 20-ml test-tubes with ground-in stoppers, the phases (5 ml of each) being mixed by a mechanical shaker in an air-bath thermostatically controlled at 25 ± 0·2°. Two methods were used for introducing PAN into the system. In the first, 0·5 ml of ethanolic PAN solution was added to a known volume of indium solution (up to 0·2 ml) and then diluted to 5 ml with buffer. An orange–red precipitate appeared in 30–60 sec; 10 min later, 5 ml of chloroform were added and the extraction was begun. In the other method, a known volume of

indium solution was diluted to 5 ml with buffer and 5 ml of a chloroform solution of PAN were added immediately, and the tube was shaken.

When the phases had separated, 0·1–0·2 ml of each phase was withdrawn and its indium content was determined by β-counting. The sample aliquot was evaporated to dryness on a steel planchette under an IR lamp, and the activity was measured with an end-window counter. In some cases the indium content of the organic phase was measured colorimetrically with an FEK-56 photocolorimeter (1-cm cells, No. 6 filter—maximum transmission at 540 mμ) against a reagent blank. A pH meter was used to measure the pH of the aqueous phase at equilibrium. The distribution ratio (E) or the degree of extraction (R) was calculated.

RESULTS AND DISCUSSION

Extraction from acetate solutions

Influence of the buffer. According to the literature[1–5] maximum formation of the PAN-indium complex occurs at pH 5·5–6·5 in acetate buffers. We studied the extraction of indium over this pH range, using acetate, biphthalate, citrate and hexamine

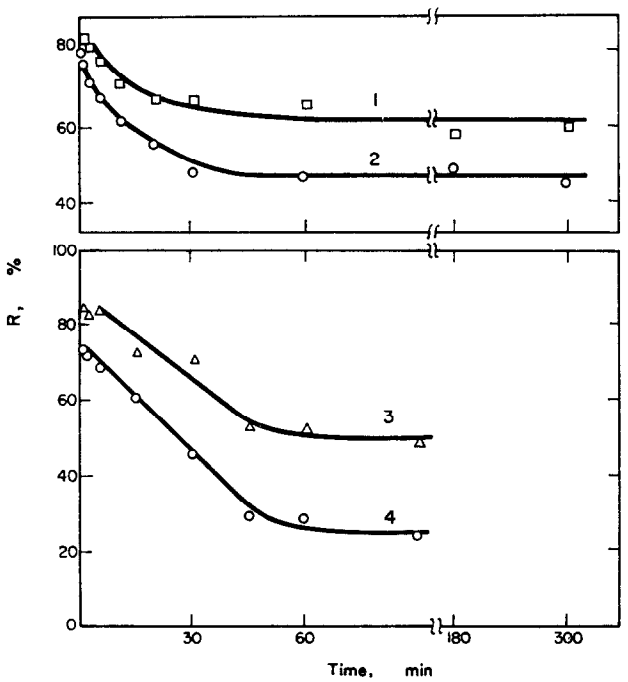

FIG. 1.—Rate of extraction of indium with PAN added in the aqueous phase.
1—$6 \times 10^{-3}M$ PAN, pH 6·0; *2*—$6 \times 10^{-3}M$ PAN, pH 5·3;
3—$1{\cdot}5 \times 10^{-3}M$ PAN, pH 6·0; *4*—$1{\cdot}5 \times 10^{-3}M$ PAN, pH 5·3.

buffers, adding ethanolic PAN solution to the indium, and extracting for 90 sec. Before extraction the concentration of indium in the aqueous phase was 2×10^{-5} M and of reagent $1{\cdot}5 \times 10^{-3}$ M. Indium was extracted best from acetate medium (90–92%), poorly from biphthalate (7–13%) and not at all from citrate media. When hexamine was used, 60% of the indium was extracted but phase separation was not very good and the radioactive measurements were unreliable; colorimetric measurements were also unsatisfactory, the absorbance of the organic phase falling rapidly with time, whereas the colour of the extract from acetate medium was stable for 1·5–2 hr. The nature of the buffer obviously influences the degree of extraction considerably, acetate being the best.

Rate of extraction. It was noticed that prolonged shaking resulted in a decrease in the degree of extraction. The kinetics of the extraction were therefore investigated with an initial indium concentration of $1{\cdot}2 \times 10^{-5}M$, PAN concentrations of $1{\cdot}5 \times 10^{-3}$, 6×10^{-3} and $3 \times 10^{-2}M$, and acetate buffers of pH 5·3, 5·9–6·0, 6·4 and 6·8. The kinetic curves obtained when PAN is added in ethanolic solution to the aqueous phase before the chloroform extraction are unusual—they pass through a maximum (Fig. 1). The precipitate initially produced is at first rapidly extracted to a high

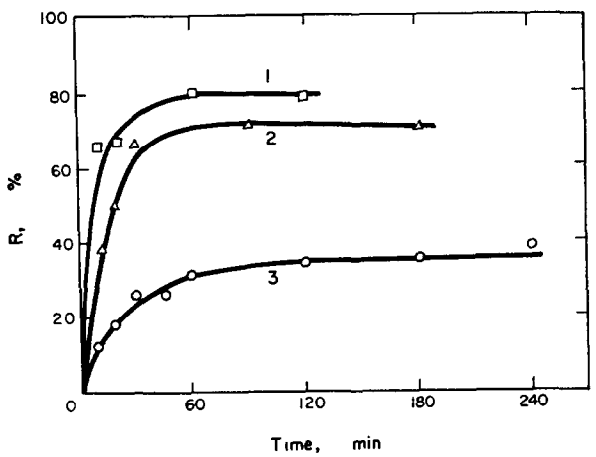

FIG. 2.—Rate of extraction of indium with various concentrations of PAN in chloroform, at pH 6·0.
1—$3 \times 10^{-2}M$; *2*—$6 \times 10^{-3}M$; 3—$1{\cdot}5 \times 10^{-3}M$.

degree by the chloroform, but after 1 or 2 min begins to return to the aqueous phase, true equilibrium being reached after about an hour. This means that in all previously published work the indium was extracted under non-equilibrium conditions and at maximum efficiency. When the PAN was added in chloroform solution, the curves were of the usual shape (Fig. 2); the rate of extraction was very slow, 1–2 hr being needed to reach equilibrium. At equilibrium, however, the degree of extraction is the same for both methods of introducing the reagent (Fig. 3). Alcohol was added to the chloroform-PAN extraction system to make conditions the same for both methods.

The higher the concentration of PAN, the faster the extraction equilibrium is established—2–3 hr for $1{\cdot}5 \times 10^{-3}M$ PAN, and less than 1 hr for 6×10^{-3} and $3 \times 10^{-2}M$ PAN. The rate of extraction seems to be independent of pH over the range 5·3–6·4 but becomes slower at higher pH values. Above pH 6·4 the radio-counting results are unreliable, especially when the equilibration times become very long.

Effect of pH and concentration of PAN. Figures 4 and 5 show the effect of pH on extraction when the PAN concentration is varied, but the acetate and indium concentrations are kept constant. The phases were shaken for 90 sec (Fig. 4) or 3 hr (Fig. 5). The results show that for short shaking-periods the degree of extraction is not much affected by the PAN concentration, and reaches a maximum at pH 6–7. For the longer shaking, the optimum pH is 6·0–6·4, and the extraction is strongly dependent on the concentration of PAN, at higher pH values the material balance is poor.

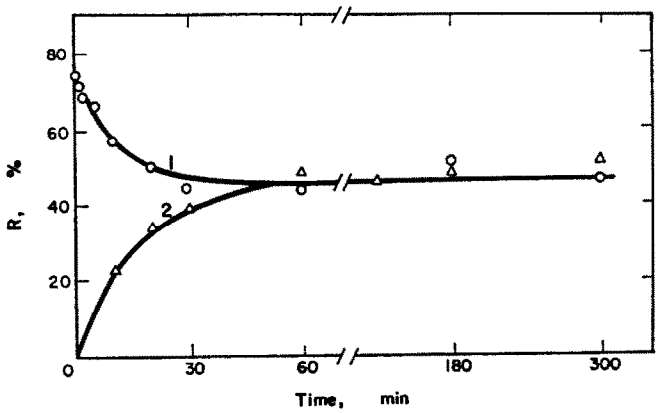

FIG. 3.—Rate of extraction with both methods of adding PAN.
1—PAN added in aqueous phase; *2*—PAN added in chloroform.

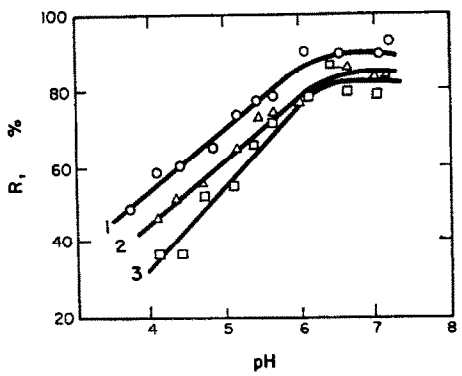

FIG. 4.—Dependence of extraction of indium on pH and on the concentration of PAN added in the aqueous phase (shaking-time 1·5 min).
1—$6 \times 10^{-3}M$ PAN; *2*—$1{\cdot}5 \times 10^{-3}M$ PAN; *3*—$3 \times 10^{-4}M$ PAN.

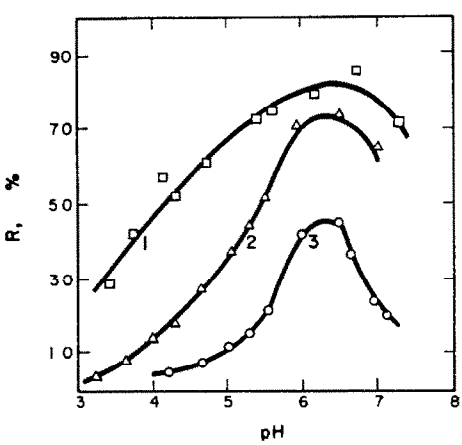

FIG. 5.—Dependence of extraction of indium on pH and on concentration of PAN added in the chloroform phase (shaking-time 3 hr).
1—$3 \times 10^{-2}M$ PAN; *2*—$6 \times 10^{-3}M$ PAN; *3*—$1{\cdot}5 \times 10^{-3}M$ PAN.

Composition of the compound extracted

Because the extraction curves obtained under equilibrium conditions (shaking for 3 hr) show strong dependence of the degree of extraction on the PAN concentration, it is not possible to use continuous variation or mole-ratio methods to determine the ratio of the components in the compound extracted. Instead, a logarithmic method[13] (based on the shift of equilibrium) was used.

Figure 6 shows the log-log plot of distribution ratio *vs.* PAN concentration for

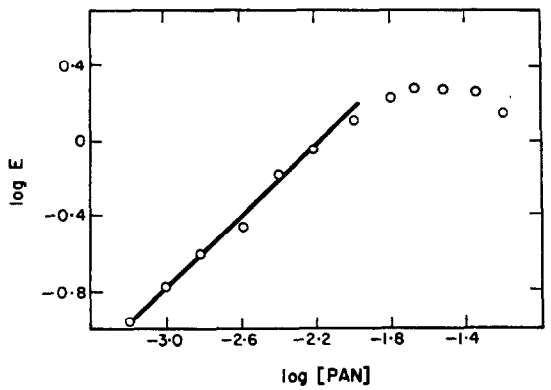

FIG. 6.—Determination of the mole ratio of indium to PAN by the equilibrium shift method.

3-hr extraction of indium ($1{\cdot}2 \times 10^{-5}M$) from acetate buffer at pH 5·5 with a chloroform solution of PAN. At this low concentration indium does not form polynuclear complexes in aqueous medium, and this was confirmed by the fact that log E was independent of the indium concentration. Because PAN was used in very large excess, its initial concentration is plotted on the graph. The ratio of indium to PAN is seen to be 1:1.

The ratio of indium to PAN in the complex extracted in non-equilibrium conditions was also studied, in this case by the methods of continuous variation and of mole ratio. An alcohol solution of PAN was added to the aqueous phase at pH 6·0 and the complex was extracted with chloroform for 90 sec. The total concentration of indium and PAN was $6 \times 10^{-4}M$ for the continuous variation method, and for the mole-ratio method the concentration of indium was $7{\cdot}4 \times 10^{-5}M$ and that of PAN was varied from $2{\cdot}4 \times 10^{-5}$ to $2{\cdot}0 \times 10^{-4}M$. The alcohol concentration was kept constant throughout. Both methods gave a 1:1 ratio for In:PAN.

Since there is only one PAN molecule associated with each indium ion, the complex must be cationic, and an anion must be involved in forming the species extracted. When the 90-sec extract was tested by the lanthanum nitrate–iodine test,[14] acetate was found in it when indium was present but not when indium was absent. Increase in the acetate concentration in the aqueous phase was found to increase strongly the degree of extraction of indium (Fig. 7) indicating indirectly that acetate is involved in the complex extracted.

Influence of anions

Various anions other than acetate were tested for their effect on the extraction of indium. In all these experiments the complex was extracted during 90 sec from a

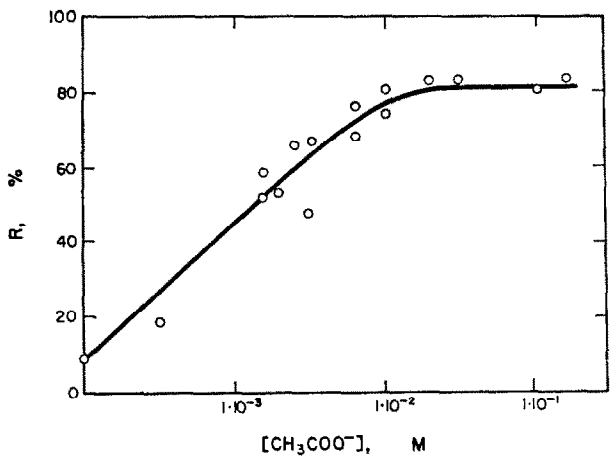

FIG. 7.—Dependence of extraction of indium with PAN on the acetate concentration. PAN added in the aqueous phase at pH 6, shaking-time 1·5 min.

solution to which PAN had been added in alcohol solution: the indium concentration was $1{\cdot}2 \times 10^{-5}M$ and the PAN was $1{\cdot}5 \times 10^{-3}M$. The anions included isobutyrate, isovalerate, caproate, chloride, perchlorate and nitrate. The organic anions were added as the free acid to an indium solution buffered with biphthalate, their concentration being $0{\cdot}14M$, and the pH was varied over the optimum range for extraction of the PAN complex. For comparison, an extraction was made with $0{\cdot}2M$ sodium acetate present in the biphthalate buffer. The inorganic anions were added as their lithium or sodium salts, extractions being made from the salt solutions with and

TABLE I.—EFFECT OF ANIONS ON EXTRACTION OF INDIUM WITH PAN FROM BIPHTHALATE BUFFER

Source of anion	pH	Extraction, %	Blank extraction,* %
Sodium acetate	6·3	21·5	
Caproic acid	5·1	75·6	3·1
	5·4	90·0	6·0
	5·7	97·5	40·0
	5·9	98·5	
Isobutyric acid	5·0	30·7	0
	5·3	40·0	0
	5·8	73·0	0·6
	6·3	86·0	0·4
Isovaleric acid	5·3	63·2	1·3
	5·5	78·0	2·8
	5·9	91·2	7·3
	6·3	97·5	10·5
Lithium chloride, $3{\cdot}6M$	4·4	68·5	
Sodium perchlorate, $3M$	4·4	53·9	
	4·7	58·2	
	5·7	55·1	0
Lithium chloride, $9M$†	5·5	37·2	6
	6·2	54·1	0
	6·7	65·0	0
	7·2	67·0	0

* In the absence of PAN.
† No buffer present.

without biphthalate buffer. In the absence of buffer the pH was adjusted by addition of 0·4*M* sodium hydroxide.

The results in Table I show that the organic anions are even more efficient than acetate in promoting the extraction of indium. Indium is also extracted well from biphthalate buffer if relatively large amounts of lithium chloride or sodium perchlorate are added. A poor material balance was obtained when the biphthalate was omitted and 5*M* solutions of the anions were used, and these results are not reported, but a good balance was obtained when indium was extracted from 9*M* lithium chloride.

Chloride was easily detected in the extracts by mercurimetric titration, with diphenylcarbazone as indicator, of the chloride found in the aqueous phase when the extract was stripped with 0·06*M* nitric acid. A blank run was made and corrected for. Attempts to determine the ratio of indium to chloride gave results which were not constant but varied between 1:1 and 1:2. It was found that under equilibrium conditions indium is not extracted with chloride as a counter-anion. The ratio of PAN to indium remained 1:1 irrespective of the anion used.

CONCLUSION

It is evident that when indium is extracted with PAN, a mixed complex is formed with a counter-anion. Similar species appeared to be formed with other metals which react with PAN in a ratio too low to produce an uncharged complex, *e.g.*, iron(III), cobalt(III), yttrium, palladium(II), rhodium(III), iridium(III).[6–9] It is significant that the extraction of these elements was studied with acetate or chloride buffers.

Zusammenfassung—Die Extraktion von Indium in Chloroform mit 1-(2-Pyridylazo)-2-naphthol (PAN) wurde eingehend untersucht. Die Extraktionsgeschwindigkeit ist an größten, wenn PAN zur wäßrigen Phase gegeben und nicht als Chloroformlösung zugesetzt wird. Das Verhältnis Indium: PAN ist 1:1 und der kationische Komplex kann nur extrahiert werden, wenn ein geeignetes Anion wie Acetat oder Chlorid anwesend ist.

Résumé—On a effectué une étude détaillée de l'extraction de l'indium en chloroforme au moyen de 1-(2-pyridylazo)2-naphtol (PAN). La vitesse d'extraction est maximale si le PAN est ajouté à la phase aqueuse et non en solution chloroformique. Le rapport de l'indium au PAN est 1:1 et l'on ne peut extraire le complexe cationique qu'en présence d'un anion convenable, comme l'acétate ou le chlorure.

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POLAROGRAPHIC STUDY OF BIS(2-PYRIDYL)DISULPHIDE DI-*N*-OXIDE AND BIS(2-QUINOLYL)DISULPHIDE DI-*N*-OXIDE IN AQUEOUS ETHANOL

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Summary—The polarographic reduction of bis(2-pyridyl)- and of bis(2-quinolyl)disulphide di-*N*-oxide in aqueous alcohol yields aryl mercaptans. The electrode reaction is kinetically controlled by an initial one-electron transfer step, and values for the transfer coefficients and the specific heterogeneous rate constants for the forward reactions are presented. The polar *N*-oxide function in the α-position withdraws electrons from the disulphide bond, making the half-wave potential less negative than that of the diphenyl disulphide. The pK_a values of the mercapto compounds formed have been evaluated and the low values obtained for the heterocyclic *N*-oxides are further evidence for tautomerism in these compounds.

IN aqueous alcohol, aromatic disulphides are polarographically reduced to aryl mercaptans.[1] The overall reaction may be written

$$\mathrm{ArSSAr} + 2\mathrm{H}^+ + 2\mathrm{e} \rightarrow 2\mathrm{ArSH}.$$

In a buffered solution, a polarographically reversible reaction of this type will give a wave in accordance with the equation

$$E = E^\circ + \frac{RT}{2F} \cdot \ln\left(\frac{i_d - i}{i^2}\right) - 0{\cdot}0591\ \mathrm{pH} + \frac{0{\cdot}0591}{2} \log\left(\frac{k_2^2}{k_1^2}\right) \qquad (1)$$

at 25°, where k_1 is the Ilkovič constant for the reactant, and k_2 for the product (ArSH), and the other symbols have their usual significance. This equation (ignoring activity coefficients) predicts that a plot of E against $\ln [(i_d - i)/i^2]$ will be linear, with slope $RT/2F$ for a reversible reaction. Furthermore, the half-wave potential will depend upon the diffusion current i_d and hence upon the disulphide concentration.

$$E_{1/2} = E^\circ + \frac{RT}{2F} \cdot \ln\left(\frac{2}{i_d}\right) - 0{\cdot}0591\ \mathrm{pH} + \frac{0{\cdot}0591}{2} \log\left(\frac{k_2^2}{k_1^2}\right). \qquad (2)$$

It has already been shown[1] that for diphenyl disulphide a plot of E against $\ln [(i_d - i)/i^2]$ is curved, whereas a plot of E against $\ln [(i_d - i)/i]$ is a straight line. Furthermore, equation (2) predicts that $E_{1/2}$ will vary with pH at all values, whereas in alkaline solutions the $E_{1/2}$ values for diphenyl disulphide are independent of the hydrogen ion concentration. The waves obtained for diphenyl disulphide are consistent with a slow rate-determining step involving the transfer of one electron to the aromatic disulphide:

$$\mathrm{ArSSAr} + \mathrm{e}^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} (\mathrm{ArSSAr})^-. \qquad (3)$$

Here, k_f and k_b refer to the heterogeneous rate constants for the forward and back reactions, respectively. If we assume that a second electron is added rapidly to the anion produced, there is still an overall two-electron transfer.

$$(ArSSAr)^- + e^- \rightarrow 2ArS^- \tag{4}$$

$$2ArS^- + 2H^+ \rightleftharpoons 2ArSH. \tag{5}$$

Once again ignoring activity coefficients we may write an equilibrium constant (K_a) for equation (5) and derive a new equation for the polarographic wave (6):

$$E = E_{1/2} - \frac{RT}{\alpha n_a F} \cdot \ln\left(\frac{i}{i_d - i}\right). \tag{6}$$

In this equation α is the transfer coefficient and n_a, the number of electrons transferred in the rate-determining step, is unity. The half-wave potential in a buffered solution is given by equation (7), but E° is not strictly the standard potential, and the terms k_1' and k_2' include kinetic factors.

$$E_{1/2} = E^\circ - \frac{RT}{\alpha F} \cdot \ln\left(\frac{k_2'}{k_1'}\right) - \frac{RT}{F} \cdot \ln\left(\frac{K_a}{K_a + C_{H^+}}\right) \tag{7}$$

Thus in buffered acid solution where $C_{H^+} \gg K_a$, the half-wave potential varies with pH, but in alkaline solution, where $C_{H^+} \ll K_a$, the half-wave potential is independent of the hydrogen ion concentration.

Kapoor and his coworkers[1] assumed this reaction sequence, but the possibility cannot be ignored that the anion might dissociate before the second electron is added. In this case, the second electron would be added to the radical formed when the disulphide ion dissociates. Unfortunately, the polarographic data do not indicate which mechanism is correct.

$$(ArSSAr)^- \rightarrow ArS^- + ArS. \tag{8}$$

$$ArS^\cdot + e \rightarrow ArS^- \tag{9}$$

EXPERIMENTAL

Apparatus

Polarograms were recorded with an Atlas Tast-Polarograph Selector D. All potentials were measured against a saturated calomel electrode at 21°. Corrections for cell resistance were very small. Pure nitrogen gas was bubbled first through the appropriate solvent to saturate the gas and then through each solution, for 30 min before the polarograms were recorded and was passed over the surface during the voltage scans.

The capillary characteristics were:

$$m = 2{\cdot}723 \text{ mg.sec}^{-1}$$

$$t = 3{\cdot}24 \text{ sec}$$

$$m^{2/3}t^{1/6} = 2{\cdot}37 \text{ mg}^{2/3}\text{.sec}^{-1/2}$$

$$h = 60{\cdot}0 \text{ cm}.$$

The pH measurements were made with a pH meter Model 23A (Electronic Instruments Ltd.), using prepared glass and calomel electrodes. In view of the solvent mixture used, these pH values must be regarded as "apparent pH."

Materials

Bis(2-pyridyl)disulphide di-N-oxide. A mixture of 2-mercaptopyridine-1-oxide (8·0 g), chloroform (50 ml) and water (50 ml), was titrated with 0·1*N* iodine in aqueous potassium iodide, with shaking

between each addition, until a red colour appeared in the chloroform layer. A few drops of 0·03*N* sodium thiosulphate were then added and the mixture was shaken. The clear chloroform layer was removed and the aqueous layer extracted with two further 100-ml portions of chloroform. The combined chloroform extracts were concentrated by evaporation, and the addition of diethyl ether gave crystals of bis(2-pyridyl)disulphide di-*N*-oxide (6·5 g, 81·4%) m.p. 200–202° (lit.[2] 200–201°), (found: C, 47·6; H, 3·1; N, 11·7%; calc. for $C_{10}H_8N_2O_2S_2$: C, 47·6; H, 3·2; N, 11·1%).

Bis(2-quinolyl)disulphide di-N-oxide. 2-Mercaptoquinoline-1-oxide (0·2 g) was oxidized with iodine solution as described above to give crystals of the bis(2-quinolyl)disulphide di-*N*-oxide (0·15 g, 75·0%) m.p. 192–194° (found: C, 61·1; H, 3·7; N, 8·0%; calc. for $C_{18}H_{12}N_2O_2S_2$: C, 61·4; H, 3·4; N, 7·9%).

Procedure

Solutions of bis(2-pyridyl)disulphide di-*N*-oxide ($6{\cdot}00 \times 10^{-4}$ *M*) or bis(2-quinolyl)disulphide di-*N*-oxide ($8{\cdot}00 \times 10^{-4}$ *M*) in 50% aqueous ethanol at different pH values (Britton-Robinson buffers) were used for polarographic measurements. In certain experiments the concentrations of disulphide were varied and in others the height of the mercury column was altered, but these are referred to specifically in the discussion.

RESULTS AND DISCUSSION

Well-defined polarographic waves were obtained for both disulphides over a wide pH range (Fig. 1), but the more alkaline solutions were unstable, rapidly becoming yellow. The polarograms were analysed by plotting log $[i/(i_d - i)]$ against potential, and half-wave potentials were evaluated from the linear plots obtained. Some waves were analysed by plotting log $[i^2/(i_d - i)]$ against potential and the curvature of these plots confirms the irreversible nature of the electrode reactions (*e.g.*, Fig. 2). The wave height was proportional to concentration, and the half-wave potential was independent of the concentration for each compound in the range studied (Table I).

For each disulphide, a plot of the half-wave potential against pH gave two

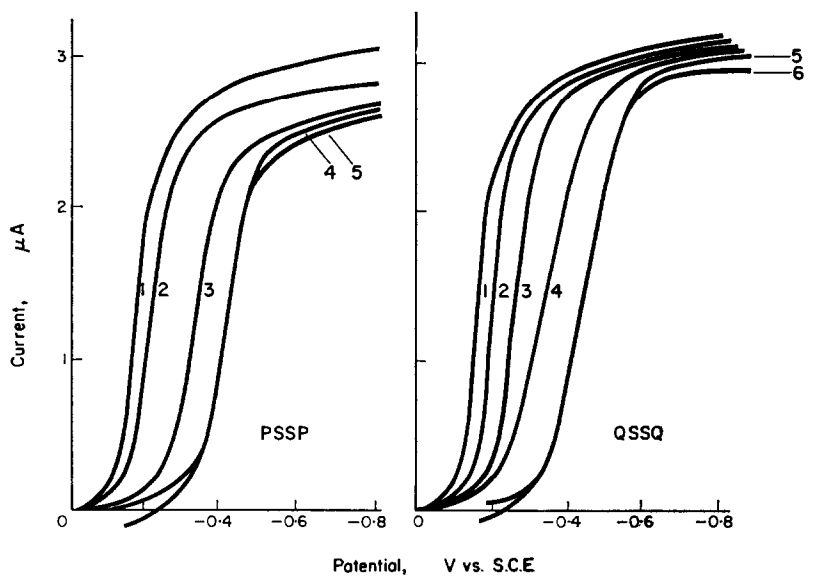


FIG. 1.—Polarographic waves for bis(2-pyridyl)- and bis(2-quinolyl)disulphide di-*N*-oxide (PSSP and QSSQ) at various pH values.
PSSP: pH, *1*—2·0; *2*—3·3; *3*—4·9; *4*—7·0; *5*—9·3. QSSQ: pH, *1*—2·0; *2*—2·4; *3*—3·8; *4*—4·6; *5*—8·5; *6*—10·0.

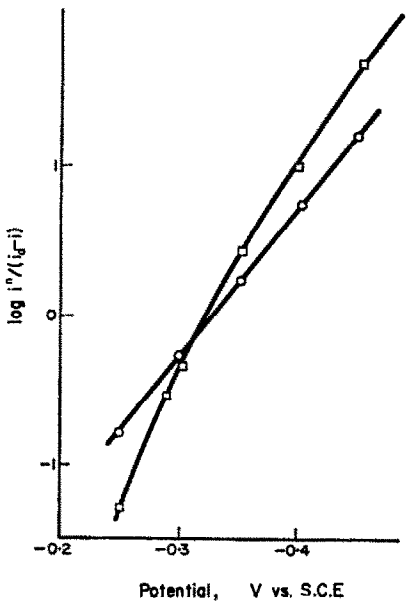


FIG. 2.—Typical plots of log $[i^2/(i_d - i)]$ (□) or log $[i/(i_d - i)]$ (○) against applied potential for bis(2-pyridyl)disulphide di-*N*-oxide.

straight lines (Fig. 3). In acid medium the slope of the line was consistent with n_a equal to unity, and in alkaline media the half-wave potential was independent of pH, [equation (7)]; thus the intersection gives pK_a for the product, *i.e.*, 6·21 for 2-mercaptopyridine-1-oxide and 6·82 for 2-mercaptoquinoline-1-oxide, in 50% aqueous ethanol.

If equation (3) is the slow rate-determining step, it is possible, by neglecting the back-reaction, to calculate the heterogeneous rate constant for the forward reaction from the relationship given by Koutecký,[3]

$$k_f = \frac{\lambda D^{1/2}}{t^{1/2}} \tag{10}$$

The values of λ for various values of the ratio i/i_d are given in Koutecký's table.[3]

TABLE I.—POLAROGRAPHIC RESULTS: EFFECT OF CONCENTRATION

Compound	C, $M \times 10^3$	i_d, μA	αn_a	$-\log k_f^\circ$	$-E_{1/2}$, V
PSSP*	0·91‡	4·1	0·45	3·76	0·33
	0·60	2·7	0·45	3·76	0·33
	0·30	1·35	0·45	3·71	0·33
	0·10	0·45	—	—	0·33
QSSQ†	0·80	3·10	0·50	4·50	0·41
	0·40	1·55	0·48	4·44	$0·40_5$
	0·20	0·75	—	—	0·41

* Bis(2-pyridyl)disulphide di-*N*-oxide.
† Bis(2-quinolyl)disulphide di-*N*-oxide.
‡ *i.e.*, 0·00091 *M*.

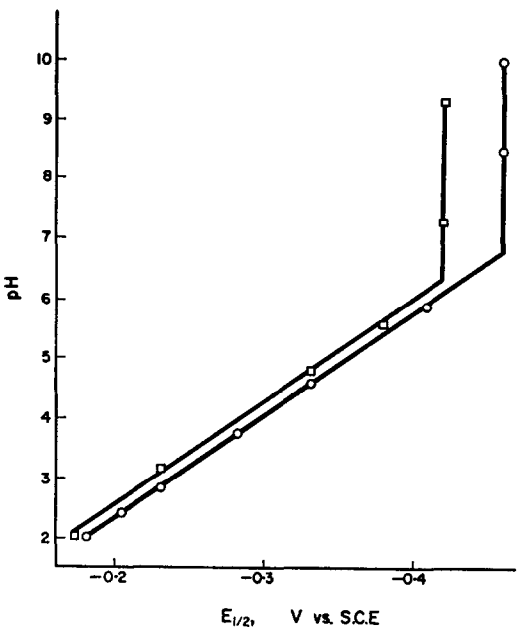


FIG. 3.—Variation of half-wave potential with hydrogen ion concentration.
□—PSSP; ○—QSSQ.

The value of D may be calculated from the Ilkovič equation assuming that n is two for the overall reaction. Here t is the drop-time. By plotting log k_f against potential for each wave (Fig. 4) we obtain log $k_f°$ (where the electrode potential is equal to that of the normal hydrogen electrode). The slope of this curve gives the value of α, the transfer coefficient (since n_a is unity).

$$\ln k_f = \ln k_f° - \alpha n_a FE/RT \tag{11}$$

The same values for the transfer coefficients are obtained by the use of equation (7) and the slope $RT/\alpha n_a F$ of the plot of E against ln $[i/(i_d - i)]$.

Rearranging equation (11) for the half-wave potential, we obtain equation (12), where $\lambda_{1/2}$ is the value of λ when i/i_d is 0·5.

$$E_{1/2} = \frac{RT}{\alpha n_a F} . \ln \frac{k_f°}{\lambda_{1/2} D^2} - \frac{RT}{\alpha n_a F} . \ln t \tag{12}$$

The variation of half-wave potential with drop-time predicted by this equation has been verified experimentally (Fig. 5) for both compounds. In one series of experiments the height of the mercury column was varied from 25 to 60 cm and the $E_{1/2}$ values were evaluated. From equation (13), where $\Delta E_{1/2}$ is the difference in half-wave potential

$$\Delta E_{1/2} = \frac{RT}{2 \times 2{\cdot}303 \alpha n_a F} . \log \frac{t_1}{t_2} \tag{13}$$

observed for drop-times t_1 and t_2 seconds, the value of $\Delta E_{1/2}$ for mercury columns 60 and 25 cm high was 20 mV and the values obtained experimentally were 20·2

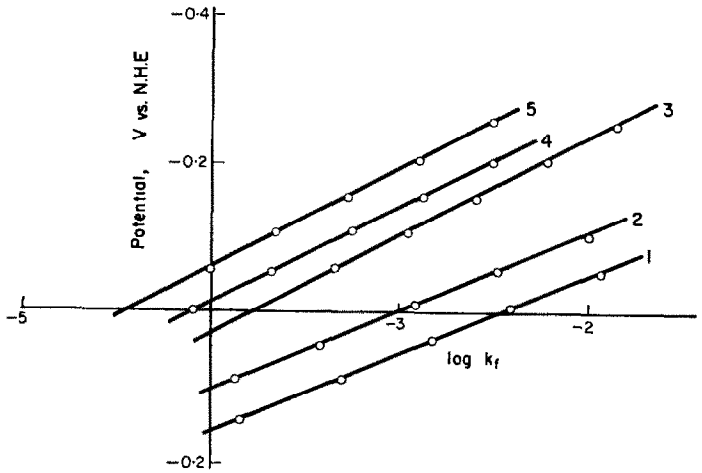


FIG. 4.—Variation of log k_f with applied potential for bis(2-pyridyl)disulphide di-*N*-oxide at different pH values.
pH: *1*—2·0; *2*—3·3; *3*—4·8; *4*—5·5; *5*—7·0.

and 21·3 mV for bis(2-pyridyl)- and bis(2-quinolyl)disulphide di-*N*-oxide, respectively. These results confirm that α and k_f° do not change with drop-time.

For the purposes of discussion it is useful to compare the results of the present work (Table II) with the results of Kapoor *et al.*[1] on diphenyl disulphide (Table III). The half-wave potentials and $-\log k_f^\circ$ values are quoted for the alkaline solutions where the product is fully dissociated. The low half-wave potentials for the *N*-oxides are attributed to the electron-withdrawing effect of the *N*-oxide function which is particularly marked in the α-position, reducing the electron density on the S—S bond. In the case of the bis(2-quinolyl)disulphide di-*N*-oxide, this effect is counteracted to a small extent by the annulated benzene ring.

The pK_a values found for these mercapto *N*-oxides are very low compared to that for thiophenol. The interaction of the *N*-oxide function with the heteroaromatic ring (resulting in a positive charge in the α- and γ-positions) is well known,[4] and

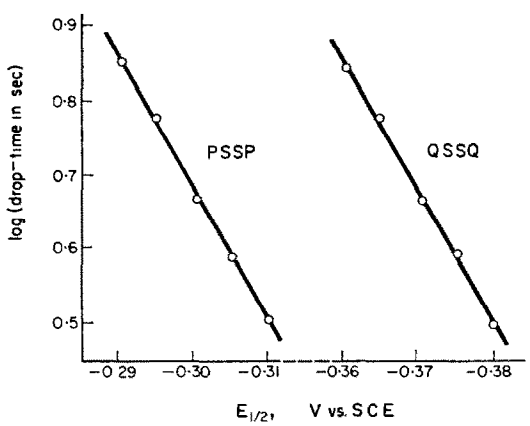


FIG. 5.—Variation of half-wave potential with drop-life.

TABLE II.—SUMMARY OF POLAROGRAPHIC RESULTS

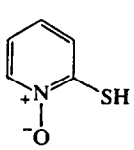
	Apparent pH	$-E_{1/2}$, *V vs.* N.H.E.	α	$-\log k_f°$
PSSP*	2·0	$0{\cdot}17_5$	0·55	2·43
	3·2	0·23	0·56	3·00
	4·8	0·33	0·45	3·76
	5·5	0·38	0·46	4·11
	7·3	0·42	0·46	4·42
	9·3	0·42	0·46	4·42
QSSQ†	2·0	0·18	—	—
	2·4	$0{\cdot}20_5$	—	—
	2·9	0·23	—	—
	3·8	0·28	0·53	3·58
	4·6	$0{\cdot}33_5$	0·45	3·90
	5·9	0·41	0·50	4·50
	8·5	0·46	0·51	4·86
	10·0	0·46	0·45	4·86

* Bis(2-pyridyl)disulphide di-*N*-oxide, $10^6 \times D = 2{\cdot}63$ cm^2.sec^{-1}.
† Bis(2-quinolyl)disulphide di-*N*-oxide, $10^6 \times D = 1{\cdot}73$ cm^2.sec^{-1}.

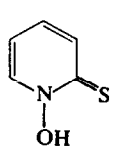
TABLE III.—COMPARISON OF RESULTS WITH DIPHENYL DISULPHIDE (DSSD)

Compound	pK_a	$-E_{1/2}$, *V vs.* S.C.E.	$-\log k_f°$ (in alkaline media)	αn_a
DSSD	8·64	0·57	6·74	0·80
PSSP	6·2	0·42	4·41	0·46
QSSQ	6·7	0·46	4·86	0·48

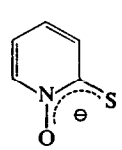
evidence has been reported that 2-mercaptopyridine-1-oxide (I) exists predominantly in the thione form (II).[5,6]



(I)



(II)



(III)

Similarly, the anion formed when 2-mercaptopyridine-1-oxide dissociates will be stabilized by charge dispersal (III). The resulting low pK_a value for 2-mercaptopyridine-1-oxide (and for 2-mercaptoquinoline-1-oxide) favours the formation of stable metal mercaptide complexes in more highly acidic solutions than for thiophenol. The results quoted for diphenyl disulphide refer to solutions in 60% v/v ethanol in water. The analytical applications of 2-mercaptopyridine-1-oxide have already been reported[6] and 2-mercaptoquinoline-1-oxide has been investigated.[7]

Acknowledgement—We wish to thank Dr. J. A. W. Dalziel for helpful and stimulating discussions, and I. E. K. thanks the University of Damascus for financial assistance during the course of this work.

Zusammenfassung—Die polarographische Reduktion von Bis(2-pyridyl)- und Bis(2-chinolyl)disulfid-di-*N*-oxid in wäßrigem Alkohol gibt Arylmercaptane. Die Elektrodenreaktion ist kinetisch kontrolliert durch eine anfängliche Einelektronenübergangsstufe; Werte der Durchtrittsfaktoren und der spezifischen heterogenen Geschwindigkeitskonstanten der Hinreaktionen werden angegeben. Die polare *N*-Oxidgruppe in Alpha-Stellung entzieht der Disulfidbindung Elektronen; dadurch wird das Halbstufenpotential weniger negativ als das von Diphenyldisulfid. Die pK_a-Werte der gebildeten Mercaptoverbindungen wurden berechnet; die bei den heterocyclischen *N*-Oxiden gefundenen niedrigen Werte geben einen weiteren Hinweis auf die Tautomerie dieser Verbindungen.

Résumé—La réduction polarographique des di N-oxydes des bis(2-pyridyl) et bis(2-quinoleyl) disulfures en alcool aqueux donne des arylmercaptans. La réaction à l'électrode est contrôlée cinétiquement par un stade initial de transfert à un électron et l'on donne des valeurs pour les coefficients de transfert et les constantes spécifiques de vitesse hétérogène pour les réactions directes. La fonction polaire N-oxyde en position α enlève des électrons de la bande disulfure, rendant le potentiel de demi-vague moins négatif que celui du disulfure de diphényle. On a estimé les valeurs de pK_a des composés mercapto formés et les faibles valeurs obtenues pour les N-oxydes hétérocycliques sont un nouvel argument en faveur du tautomérisme de ces composés.

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INSTRUMENTAL ACTIVATION ANALYSIS OF VEGETABLE TISSUE

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Summary—A non-destructive method for the determination of bromine, manganese, phosphorus, potassium, sodium and zinc in plant tissue by neutron activation and gamma-ray spectrometry is described. Phosphorus and potassium have been determined also by beta-counting. The method should be especially attractive for analysis of manganese and zinc.

ACTIVATION analysis, besides being a very sensitive method for the determination of trace elements, has also proved its usefulness as a rapid non-destructive technique. The combination of neutron activation and gamma spectrometry without any intermediate chemical separation step has found applications in numerous cases. The use of beta-counting in non-destructive analysis has also been successfully demonstrated.[1,2] In the present work applications of the purely instrumental neutron activation analysis to vegetable tissue are shown. The material selected for this investigation was leaves of Norway Spruce (*Picea abies*), which is an important raw material in paper manufacturing. The experience gained in this work can, however, undoubtedly be applied to a great variety of plant material samples.

EXPERIMENTAL

Counting equipment

A 400-channel gamma-spectrometer with a well-type 3 in. × 3 in. NaI(Tl) detector was used in the gamma measurements. For the beta measurements a Geiger–Mueller counter with conventional shelf arrangement was used. The window thickness of the tube was 10 mg/cm^2, and the effective diameter was 28 mm.

Irradiation

Samples of about 100 mg, dried at 50° for 24 hr, were weighed into polyethylene ampoules and irradiated for 2 days in the reactor JEEP I (Kjeller, Norway) at a thermal neutron flux of about 2×10^{12} n.cm^{-2}.sec^{-1}. After the irradiation the samples were mounted on cardboard sample holders for activity measurements. Together with the samples silica ampoules were activated, each containing 1 ml of a standard solution of an element to be determined. From each silica ampoule two 0·100-ml aliquots of the standard solution were adsorbed on diameter 20-mm filterpapers, dried carefully under a heating lamp and mounted for counting in the same way as the samples.

The standard solutions were prepared by dissolving accurately known amounts of *pro analysi* chemicals in water or dilute hydrochloric acid. The chemicals used and the approximate concentration of each standard solution are listed in Table I.

Activity measurements

The gamma-spectra of the samples were recorded at intervals after the end of the irradiation, as indicated in Fig. 1. The half-life of the different radionuclides were checked by repeated measurements.

The areas under the photopeaks were evaluated according to the method of Covell.[3] Data giving a more detailed description of the determination of each element are listed in Table 1.

As the measurement of the 1·52 MeV photopeak of ^{42}K is somewhat disturbed by the 1·37 MeV peak of ^{24}Na, the contribution of the latter nuclide was removed by "stripping" of the 2·75 MeV peak with a pure ^{24}Na source, before the amount of potassium was calculated.

The gamma-spectrometric measurement of ^{32}P was made possible by detection of the bremsstrahlung produced by the high energy beta-particles, and was based on the sum of counts accumulated in 5 channels (10 keV/channel) of the corresponding region in the gamma-spectrum. The observed count rates proved to decrease according to a pure ^{32}P decay for a period of at least 30 days. To detect possible variation in count rate due to channel drift, the phosphorus standard was counted at

TABLE I.—DATA FOR THE DETERMINATION OF EACH ELEMENT

	Br	K	Mn	Na	P	Zn
Radioisotope used	^{82}Br	^{42}K	^{56}Mn	^{24}Na	^{32}P	^{65}Zn
Half-life	35·9 hr	12·5 hr	2·58 hr	15·0 hr	14·3 d	245d
Type of measurement	γ	β,γ	γ	γ	β,γ	γ
Gamma-energy measured (MeV)	0·78	1·52	0·84	2·75	Brems-strahlung	1·11
Maximum beta-energy (MeV)	0·465	3·58	2·81	1·39	1·71	—
Time elapsed between end of irradiation and start of measurements	5–6 d	24–30 hr*	2–5 hr	24–30 hr	14 d	14 d
Substance used for the preparation of standard solution	KBr	K_2CO_3	Mn	Na_2CO_3	H_3PO_4	Zn
Approximate concentration of standard solution (mg/ml)	0·1	5	0·2	0·1	5	1

* The beta-counting of ^{42}K was postponed until 50 hr after the end of the irradiation, to avoid any contribution from ^{56}Mn.

intervals during the measurement of each series of samples. When gamma-measurements of ^{32}P and ^{65}Zn were to be performed, the samples and standards had to be transferred from the cardboard sample holders into glass vials and counted in the well of the NaI crystal in order to yield a sufficiently high sensitivity for the zinc determinations, and to give a higher and more reproducible ^{32}P bremsstrahlung production.

In the beta-measurements aluminium absorbers were used to take advantage of the high energy beta-rays of ^{42}K and ^{32}P compared to other induced activities with similar half-lives. In the ^{42}K measurements each sample was counted with two absorbers of thickness respectively 700 and 1700 mg/cm^2, the first one to discriminate beta-particles mainly due to ^{24}Na and ^{32}P, the second one to correct for counts due to gamma-rays. The difference between the two count rates was used to determine the amount of potassium present. In the ^{32}P measurements an absorber of 100 mg/cm^2 was used to discriminate possible contribution from low energy beta-emitters such as ^{35}S. The count rate due to gamma-rays was found to be negligible in this case. The results for both potassium and phosphorus were confirmed by repeated beta-measurements.

The measurement of ^{42}K by beta-counting could not be started until the activity of ^{56}Mn had decayed to a negligible level. In the same way the measurement of ^{32}P was dependent on the decay of ^{42}K.

RESULTS AND DISCUSSION

The present investigation includes analyses of 20 different samples. Each sample was divided into two aliquots which were activated and analysed separately. A summary of the results is given in Table II. The concentration range found for each element is given, and the relative standard deviation in the determination of the various elements calculated from the duplicate analyses are presented as a measure of the reproducibility of the method.

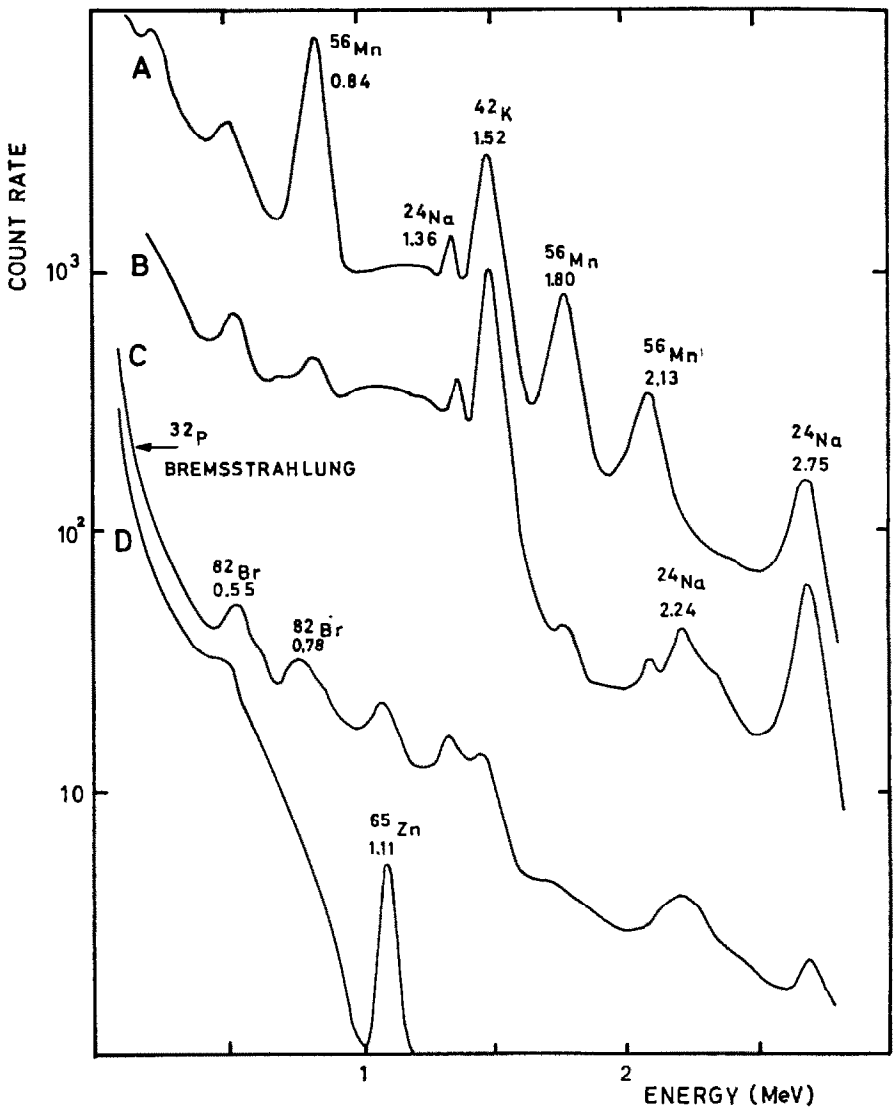

FIG. 1.—Gamma spectra of irradiated sample recorded at intervals after the end of the irradiation
A—10 hr; B—27 hr; C—6 days; D—14 days.

TABLE II.—RESULTS FOR DUPLICATE ANALYSIS OF 20 SAMPLES, BASED ON GAMMA-SPECTROMETRY

Element	Concentration range	Relative standard deviation
Br	1·0–5·2 ppm	9·3%
K	0·37–0·69%	2·7%
Mn	182–812 ppm	2·0%
Na	4–20 ppm	—
P	0·26–0·45%	2·4%
Zn	30–180 ppm	4·7%

Duplicate determinations of sodium showed a fairly wide spread, although determinations of this element by the present method are usually precise to ±5%. This is probably due to external contamination from the pre-irradiation treatment of the samples.

An investigation of the accuracy of the method was rendered possible by analysing solutions containing the elements of interest in known concentrations, in a similar way to the vegetable samples. Two different solutions with similar composition to

TABLE III.—ANALYSIS OF SOLUTIONS OF KNOWN COMPOSITION

	Element	Amount added, μg	Amount recovered, μg							
			γ-counting				β-counting			
Solution I	K	500	492	504	502	489	500	512	515	505
	Mn	50·0	50·8	50·2	48·3	50·0				
	Na	4·6	7·0	7·1	6·9	7·1				
	P	500	489	486	488	493	500	508	507	503
	Zn	20·0	20·7	20·7	20·3	21·2				
Solution II	K	400	395	403	398	406	409	396	392	389
	Mn	25·0	24·8	25·3	25·1	25·2				
	Na	9·2	12·1	11·8	11·9	12·2				
	P	250	237	246	243	244	247	258	263	260
	Zn	10·0	10·3	10·6	10·3	10·1				

the spruce samples were prepared, and four aliquots of each solution were analysed separately. The results are listed in Table III. Except in the case of sodium the agreement between the amounts added and found is very satisfactory. The reason for the high sodium values found is evidently that additional amounts of Na have been introduced during addition of the other elements.

TABLE IV.—COMPARISON OF POTASSIUM AND PHOSPHORUS CONTENTS DETERMINED BY BETA-COUNTING AND GAMMA-SPECTROMETRY

Sample No.	Potassium content %		Phosphorus content %	
	β	γ	β	γ
1	0·396	0·412	0·281	0·292
2	0·375	0·384	0·317	0·339
3	0·478	0·492	0·314	0·326
4	0·361	0·395	0·297	0·309
5	0·458	0·486	0·322	0·344
6	0·500	0·501	0·313	0·323
7	0·367	0·369	0·264	0·286
8	0·491	0·487	0·357	0·371
9	0·496	0·515	0·304	0·323
10	0·630	0·653	0·269	0·283
11	0·704	0·739	0·424	0·433
12	0·587	0·586	0·346	0·348
13	0·543	0·526	0·255	0·263
14	0·618	0·633	0·336	0·343
15	0·530	0·560	0·377	0·383
16	0·402	0·409	0·389	0·383
17	0·572	0·614	0·371	0·376
18	0·406	0·408	0·267	0·269
19	0·650	0·722	0·436	0·451
20	0·556	0·599	0·406	0·422

In Table IV is shown a comparison of results for potassium and phosphorus obtained by beta- and gamma-measurements of the same samples. In both cases the results based on measurements of gamma-rays are about 3% higher on average. The reason for this discrepancy is not obvious. One possible source of error yielding low results might be self-scattering and self-absorption of beta-particles in the irradiated needles. The results from the gamma-activity measurements of ^{32}P are probably high owing to gamma-rays or bremsstrahlung from other long-lived nuclides present in small amounts.

Systematic errors are not expected to influence the present results seriously. Neutron shielding effects are negligible since neither samples nor standards contain significant amounts of strong neutron-absorbing elements. Errors due to different counting geometry of samples and standards are assumed to be 1% or less. Interference from competing nuclear reactions is insignificant, except in the case of phosphorus, as ^{32}P is also being produced from sulphur and chlorine by (n, p) and (n, α) reactions respectively. The fast neutron flux in the irradiation position was, however, low compared to the thermal flux. The ^{32}P activity produced by irradiation of 1 mg of phosphorus was 55 times as great as the activity of 1 mg of sulphur irradiated simultaneously, and the corresponding figure for chlorine was 250. As no values for the normal content of sulphur and chlorine in Norway Spruce seem to be available, it is difficult to establish the corrections necessary in this work. However, if sulphur and chlorine are assumed to be present in concentrations of the same order of magnitude as phosphorus, the interference is relatively small.

From the observed results and the preceding discussion the accuracy of the determination of manganese by the present method is likely to be about $\pm 3\%$. The determination of zinc is most probably accurate to $\pm 10\%$ or even $\pm 5\%$ if the activation period is increased to 4–5 days. The present method should hence be very well suited for the determination of manganese and zinc in vegetable material.

The determination of potassium is probably accurate to $\pm 5\%$ for both beta- and gamma-measurements. The same should be the case for phosphorus if a well thermalized neutron flux is employed and the contents of sulphur and chlorine are low and approximately known. The precision obtained in the determinations of phosphorus and potassium is perhaps not especially remarkable compared to conventional methods. It should be noted, however, that a large number of samples can be analysed within a short time, especially if computer technique is used for the resolution and evaluation of the gamma-spectra. The simplicity of the beta-measurements should also make this particular technique attractive for further application. The determination of manganese is also readily done by gross beta-counting through an aluminium absorber if a correction for the ^{42}K activity is introduced, or even by integral gamma-counting.

On the basis of the present work it seems unquestionable that instrumental neutron activation analysis in many cases will be a valuable supplement to methods more commonly used in chemical analysis of vegetable tissue.

Zusammenfassung—Eine zerstörungsfreie Methode zur Bestimmung von Brom, Mangan, Phosphor, Kalium, Natrium und Zink in Pflanzengewebe durch Neutronenaktivierung und Gamma-Spektrometrie wird beschrieben. Phosphor und Kalium wurden auch durch Beta-Zählung bestimmt. Die Methode sollte besonders zur Mangan- und Zink-Bestimmung von Vorteil sein.

Résumé—On décrit une méthode non-destructive de dosage du brome, du manganèse, du phosphore, du potassium, du sodium et du zinc dans le tissu végétal par activation de neutrons et spectrométrie aux rayons gamma. On a également dosé le phosphore et le potassium par comptage beta. La méthode devrait être spécialement intéressante pour l'analyse du manganèse et du zinc.

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SOME ASPECTS OF THE REACTIONS BETWEEN SELENIUM-CONTAINING LIGANDS AND PLATINUM GROUP METALS

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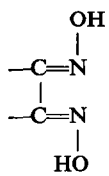
Summary—2-(2-Pyridyl)benzo[*b*]selenophene has been investigated as a possible reagent for palladium. From a consideration of its reactions with diverse metal ions, and the probable structure of the complex formed between the compound and palladium(II) it is postulated that the group —Se⋯C⋯C⋯N— may be highly selective for palladium. From the experimental evidence it is suggested that the delocalization of the metal electron density by π-bond formation between the palladium and selenium atoms is a major factor in determining the stability of the chelated complex.

THE problem of designing a reagent which is either specific for one metal or is selective for a very small number of metals, is one which has beset analytical chemists for some time. In general there are a few atomic groupings which are relatively selective; such a group is the vicinal dioxime group



which is selective for nickel and palladium. This group can be made more selective[1,2] by alteration of the N—C—C angles so that the distance between the terminal ligand nitrogen atoms is more suited for the accommodation of palladium than for nickel. Not only these angles but also the nature of the terminal atoms is important. The grouping ⋯N⋯C⋯C⋯N⋯ arranged in a definite pattern as in 1,10-phenanthroline is reasonably selective for a few metals. However, if the ligand atoms are altered as in —N—C—C—O— (in 8-hydroxyquinoline) or —N—C—C—S— (in 8-thiolquinoline) then the metals which may be chelated vary from compound to compound.

It was decided to investigate the replacement of one of the nitrogen ligand atoms with selenium and simultaneous fixing of the —N—C—C—Se angles so that only ions of a certain radius could form a chelate without undue deformation and deviation from the usual interatomic spacings. From a consideration of the compounds containing this grouping, we decided to investigate those containing selenium as a heteroatom in an organic molecule.

Only a few organic molecules containing selenium have been reported as forming compounds with metals, and these have been reviewed by Livingstone.[1] Some, such

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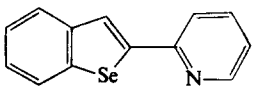
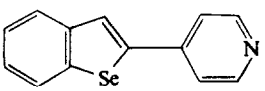
as *N'*-benzoyl-*N*-phenylseleno-urea,[2] *N'*-benzoyl-*N*-*N*,diethylseleno-urea,[2] 3,4-benzo-1',2',5'selenodiazole,[3] phenoselenazine,[4] 2-selenophene-*trans*-aldoxime,[5] and tetrahydroselenophene,[6] form addition compounds not necessarily involving a selenium-metal bond; 2,5-dibenzoyl-3,4-dihydroxyselenophene[7] forms chelates not involving selenium–metal bonds; a dialkylselenide had been reported as forming a Pt–Se bond.[8] Only a few compounds (quinoline-8-selenol)[9] and dialkyldiselenocarbamates[10] have so far been reported to form chelate compounds involving a selenium–metal bond.

We have examined a series of compounds containing the atomic grouping ··N··C··C··Se·· in an attempt to evaluate the potential of this type of compound as an analytical reagent and to elucidate the structure of the metal–organic complex formed.

The parent compound (2-selenophene-*trans*-aldoxime) containing the grouping, gives an addition compound with palladium which does not contain a Pd–Se bond.[5] However, consideration of orbital distributions and steric models indicated that a Pd–Se bond and chelate formation were probable if a reaction occurred between palladium or platinum and 2-(2-pyridyl)benzo[*b*]selenophene (I).



(I)



(II)

For comparison purposes, this compound and its isomer 2-(4-pyridyl)benzo[*b*]-selenophene (II) were prepared and investigated. The '4' isomer (II), is not capable of forming a chelate with platinum or palladium, and hence a critical comparison of any complexes of platinum or palladium formed by (I) and (II) should be possible.

EXPERIMENTAL

Preparation of the organic reagents

The organic reagents were prepared by a slight modification of the method of Buehler *et al.*,[11] using 2-stilbazole and 4-stilbazole as the starting compounds for (I) and (II) respectively. The purity and composition were determined by standard analytical procedures. The reagents were used as a 0·5% w/v ethanolic solution.

Reactions of (I) and (II) with diverse ions

The reactions of the reagents (I) and (II) with solutions of 35 metal ion species were investigated at pH 2–2·5. Higher pH values were not investigated owing to the very low solubility of reagent (I) at pH >2·5.

To 1·5-ml portions of the metal ion solutions (containing 5 mg of the ion per ml) were added 1-ml portions of the reagent solution. The mixtures were agitated at room temperature (*ca.* 23°) for 15 min and then heated at 80° for a further 15 min. The ions investigated were Al, Be, Ce(III), Cu(II), Fe(II), Pb(II)*, Hg(II), Pd(II), Rh(II), Tl(I)*, Sn(IV), V(V), As(III), Bi, Cr(III), Ir(III), Fe(III), Mn(II), Ni, Pt(II), Ru(IV), Th, Ti(IV), Zn, Ba, Cd, Co(II), Ir(IV), La, Hg(I)*, Os(IV), Pb(IV), Ag*, Sn(II) and U(IV). Hydrochloric acid was used to adjust the pH of the solutions, except in the cases marked *, where nitric acid was used.

Only palladium(II), platinum(II) and platinum(IV) and osmium(IV) gave observable reactions.

Complexes with compound(I)

Palladium(II). A primrose yellow precipitate was obtained from a cold solution, and when hot solutions were mixed. The precipitate formed within a few seconds of the mixing of the reactants.

Platinum(II). A yellow precipitate was formed in both hot and cold solutions. Platinum(II) produced *in situ* by the reaction of platinum(IV) and hydroxylamine reacted similarly.

Platinum(IV). Heating for 15 min produced a brown complex similar in appearance to the Pt(II) complex.

Osmium(IV). A dark red crystalline compound formed slowly from cold solutions. On heating, the precipitate dissolved. It recrystallized on cooling

Complexes formed with compound(II)

Yellow crystalline precipitates were obtained with Pd(II), Os(IV) and Pt(II). The precipitates formed slowly in cold solutions, but not at all in hot solutions. The precipitates dissolved on boiling and recrystallized on cooling.

The nature and composition of the complexes

Palladium(II) complex of compound(I). The reactions of the compound and its behaviour under electrophoresis at 400 V at room temperature, indicate that the compound is non-ionic. The chlorine is probably covalently bound to the palladium. It is not readily replaceable by other atoms. Silver ions do not precipitate the chloride, except on prolonged boiling. A sample of the compound was analysed for palladium (after wet oxidation) gravimetrically, with indane-1-one-2-oxime.[12] The carbon, hydrogen and nitrogen were determined by normal combustion methods. The selenium was determined iodimetrically after combustion of the compound by an oxygen-flask method, and was also calculated from the carbon content, since these two elements must be present in the same ratio as in the pure reagent. Se = 17·95% by titrimetry; Se = 18·15% by calc. The chloride content was determined coulometrically after removal of the selenium as the element. The results were C 35·9%, H 2·1%, N 3·3%, Se 18·0%, Cl 16·0%, Pd 24·5%, and indicate that the compound has an empirical formula $C_{13}H_9NSePdCl_2$. Attempts to obtain a molecular weight by cryoscopic and ebullioscopic methods were not successful.

Platinum(II) complex. Preliminary results on this compound indicate that it is similar to the palladium compound.

Osmium complex. A sample of the red "complex" heated at 110° for 1 hr became yellow. On exposure to the atmosphere for a short time it gradually regained its red colour and its original composition. Analysis showed the red material to be a hydrate of empirical formula $(C_{13}H_{10}NSe)_2OsCl_6 \cdot 2H_2O$. The loss in weight at 110° corresponds to the loss of the two water molecules. The reactions of the compound and its behaviour under electrophoresis indicate that it is an ionic salt of the type $[(RH)_2]^{2+}[MX_6]^{2-}$ (where R is a monoacidic base). Silver ions precipitate the chloride from a hot solution.

Palladium(II) complex of reagent(II)

The complex was decomposed by boiling with 0·1*M* EDTA to complex the palladium. Addition of sufficient 2*M* nitric acid to dissolve the precipitated reagent and a slight excess of silver nitrate allowed the chloride to be determined gravimetrically.

Carbon, hydrogen and nitrogen were determined by suitable combustion methods. The selenium content was calculated from the carbon content. The palladium was determined gravimetrically on a separate sample, after wet oxidation. The results, C 44·9%, H 2·7%, N 4·0%, Pd 15·3%, Cl 10·1%, Se 22·7%, give an empirical formula $PdC_{26}H_{18}N_2Se_2Cl_2$, which corresponds to Pd R_2Cl_2 where R is 2-(4-pyridyl)benzo[*b*]selenophene.

Investigation of the possible use of (I) for determination of palladium(II)

General procedure. An aliquot of the palladium(II) solution (25 ml containing 5 mg of palladium and standardized[12,18]) was diluted to 100 ml with distilled water. After adjustment of the pH to the required value by the addition of hydrochloric acid or sodium acetate and acetic acid, the samples were heated to 80 ± 1° in a water-bath. The reagent was then added dropwise with stirring. After digestion the precipitate was collected on a porosity-4 sintered glass crucible, and washed first with 0·1*M* hydrochloric acid and then with water until the washings were free from chloride. Thermogravimetric analysis and differential thermal analysis showed that 110° was a suitable temperature for drying the complex.

Variation of the pH of precipitation, A 10% excess of reagent was used, and the precipitate was digested at 80° for 30 min. Above pH 3·0 the precipitate would not coagulate unless chloride ions (from sodium chloride) were added to the reaction mixture. The effect of the addition of sodium chloride was investigated separately. The results (Table I) indicate that in the absence of sodium chloride precipitation is not quantitative at any pH. The maximum recovery occurred at pH 1·4.

TABLE I.—THE EFFECT OF VARIATION OF pH

pH	0·5	0·7	0·9	1·0	1·4	1·8	2·2	2·6	3·0
Recovery, %	42·0	73·2	89·8	91·8	92·8	92·5	90·8	89·4	87·1

The residual palladium in the filtrate was determined gravimetrically with indane-1-one-2-oxime[1] or 3,3-diphenylindane-1,2-dioxime.[13] It was found that the palladium recovered from the filtrate, when added to the original palladium recovery, gave a total of 100 ± 0·2%.

Variation in the amount of reagent. Precipitation was done at pH 1·4 with digestion for 30 min at 80 ± 1°. The palladium recovery increased as the amount of reagent was increased (Table II). Simultaneously, it became more difficult to wash the precipitate free from coprecipitated reagent.

TABLE II.—EFFECT OF VARIATION IN THE AMOUNT OF PRECIPITANT

Reagent excess, %	10	30	50	100
Palladium recovered, % (average of 3 determinations)	92·8	94·3	95·7	97·7

Variation in the time of digestion. Precipitation was achieved with 10% excess of reagent at 80° and pH 1·4. The results shown in Table III indicate that the palladium recovery increases with the time of digestion up to 30 min.

TABLE III.—EFFECT OF ALTERING THE DIGESTION TIME

Time of digestion,	0·25	0·5	0·75	1·0	24
Palladium recovered, %	84·5	92·8	92·8	92·8	93·8

The effect of addition of chloride. Precipitation was done with 10% excess of reagent with digestion for 30 min at 80° ± 1°. The pH range investigated was from 2·2 to 5·0. At the higher pH values the reagent precipitated as a white emulsion, but on digestion at 80° the yellow complex was gradually formed, but prolonged washing with 0·1*M* hydrochloric acid was necessary to remove excess of reagent. The results shown in Table IV indicate that quantitative recoveries of palladium(II) are obtained at pH 4·0–5·0 when large amounts of chloride ion are added to the reaction mixture.

TABLE IV.—DEPENDENCE OF PALLADIUM RECOVERY ON pH AND THE AMOUNT OF SODIUM CHLORIDE ADDED

pH	Palladium recovered, %			
NaCl added, *g*/5 *mg* Pd	0	1	2	5
2·2	90·8	92·3	95·5	96·6
4·0	—	100·6	100·0	100·4
5·0	—	100·5	101·2	100·8

Effect of the addition of sequestering agents. It was found that in the pH range 0·5–5·0 hydroxylamine, ammonia and EDTA completely inhibit precipitation of the complex.

The reaction of 2-(2-*pyridyl*)*benzo*[b]*selenophene with platinum(II)*

Preliminary investigations have shown that the complex formed with platinum(II) is considerably more stable than the corresponding palladium(II) complex. The platinum(II) complex is precipitated in the presence of the sequestering agents mentioned above. It has been possible to precipitate the

platinum(II) complex from homogeneous solution by *in situ* formation of Pt(II) by reduction of platinum(IV).

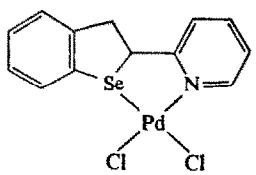
These reactions with platinum are under investigation and will be reported in a later communication

DISCUSSION

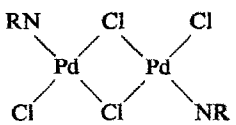
The work done shows that 2-(2-pyridyl)benzo[*b*]selenophene is of limited value as an analytical reagent for palladium. It is nevertheless of use in the general study of ligands containing selenium donor atoms, and in elucidation of their analytical chemistry.

Structure of the palladium complex of 2-(2-*pyridyl*)*benzo*[b]*selenophene*

The complex of empirical formula $C_{13}H_9NSePdCl_2$ can be represented by one of the following structures:



(III)



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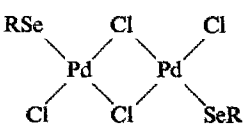

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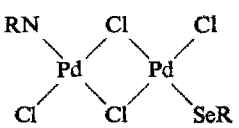
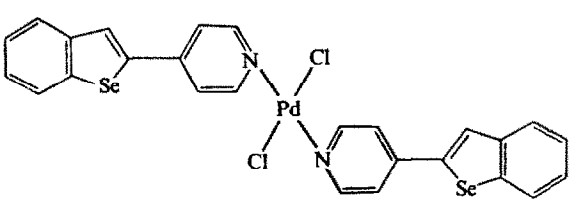


(VI)

If the reagent acts as a monodentate ligand it is probable that Pd—N bonds will be formed. If this were the case, then it would be expected that the complex would have same empirical formula as the Pd(II) complex of 2-(4-pyridyl)benzo[*b*]selenophene.

The empirical formula of the latter complex is $PdC_{26}H_{18}N_2Se_2Cl_2$ and by analogy with known palladium(II) complexes with nitrogen-containing heterocyclic monodentate ligands such as pyridine, its structure is probably



(VII)

Thus we conclude that the compound 2-(2-pyridyl)benzo[*b*]selenophene is probably not acting as a monodentate ligand, but as a bidentate one [structure (III)].

The ultraviolet, infrared and nuclear magnetic resonance spectra of the reagent and the complex were investigated (in ethanol for u.v., in deuterochloroform for NMR).

The infrared spectra give no useful information, but the ultraviolet spectra of $10^{-4}M$ ethanol solutions of the reagent and the palladium(II) complex indicate that there is a great deal of similarity between the two. The main difference is an absorption peak at about 400 mμ which is attributed to Pd bonding (Fig. 1).

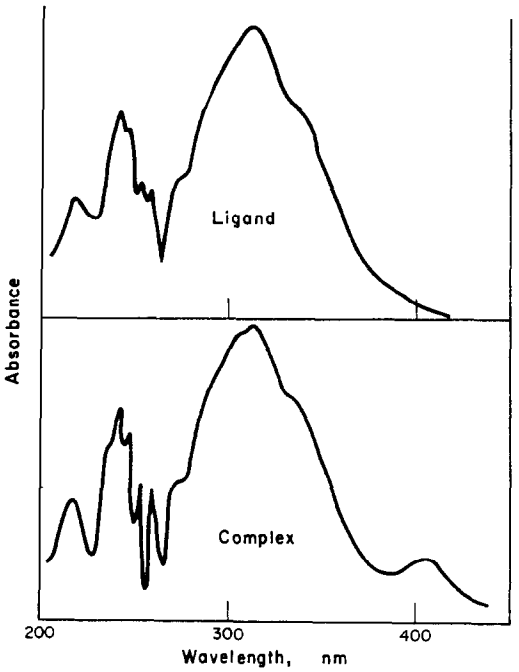


FIG. 1.—Ultraviolet absorption spectra of 2-(-2pyridyl)benzo[*b*]selenophene and its palladium(II) complex.

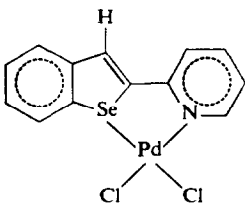
There is virtually no loss of resonance in the complex, which must, therefore have a planar configuration similar to that of the reagent. Consideration of the possible electronic structures of the complex indicates that a planar complex is possible.

The aromaticity of thiophene has been explained by Longuet-Higgins[14] who suggested that in bonding to carbon the sulphur atom uses two sp^2 hybrid orbitals to form sigma-bonds and two pd^2 hybrid orbitals to form pi-bonds. Thus the sulphur atom is left with an sp^2 "lone-pair" of electrons and an empty pd^2 hybrid orbital, both of which are oriented away from the aromatic ring, the lone-pair being in the plane of the ring, *i.e.*, in a direction suitable for σ-bond formation with a metal atom, and the pd^2 hybrid orbital normal to the plane of the ring, thus being oriented for π-bond formation.

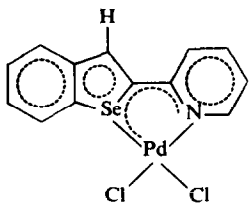
Since thiophene and selenophene are very similar in their chemical properties, and the only major constitutional difference between them is their hetero-atoms, which are of equivalent electronic structure, it may be assumed that they are of equivalent electronic structure. We therefore suggest that in the palladium(II) complex, the bond between the selenium and the palladium is formed by the selenium atom forming a σ-bond with the palladium by means of its $4s4p^2$ lone-pair electrons, accompanied by the formation of a π-bond by "back-donation" of electrons from the $4d_{(x^2-y^2)}$ orbital of palladium into the vacant $4p4d^2$ hybrid orbital of the "aromatic" selenium. In a review[15] of the criteria for π-bond formation by back-donation from the metal atom of the ligand atom, it is suggested that the availability of orbitals of similar energy is essential for the formation of such bonds; one of the main disadvantages of the theory is that to obtain this similarity of energy with nitrogen or phosphorus

which do not have 4*d* orbitals, it is often necessary to postulate a raising of the energy of the available orbitals by the difference in the electronegativities of the two atoms. In the case of selenium and palladium it is not necessary to make this qualifying assumption. The probability of bond formation is also increased if there is maximum overlap of the orbitals concerned in the bonding. Coates[16] has suggested that π-bond formation occurs *via* a vacant *d* orbital of sulphur or selenium in aliphatic molecules, and that the overlap is sufficient to give stability to the bond. In the case of thiophene, selenophene and related compounds, we suggest that since the π-bond is formed by using a pd^2 hybrid orbital which is more localized in the required region of space than is a *d* orbital, then greater orbital overlap should be obtained, resulting in a stronger bond. One of the main reasons for postulating π-bond formation in metal complexes is the need to suggest delocalization of the electron density around the central metal atom. In the case of complexes of aromatic selenium compounds in general and this particular compound in particular, if π-bonding does occur, delocalization can occur throughout the coplanar molecule as indicated in structure (IX).

It can be seen that if the molecule is not planar, then the delocalization or resonance found in the reagent would disappear and hence the spectra of the reagent and the complex would be vastly different. It was hoped that NMR studies of the nature of the 3-H atom of the selenonaphthene unit would give further evidence for the existence of the Se–Pd bond since it was thought that in the structure (VIII) the 3-H atom is likely to be more aliphatic—or less aromatic—than in structure (IX), if π bonding does not occur.



(VIII)



(IX)

The NMR studies with an HR 100 Varian Spectrometer were somewhat hindered by the insolubility of the metal complex in the normal solvents. Solvents which dissolve the complex often do so by exchange of ligand and are thus not considered suitable. A spectrum obtained by summing 200 runs for a saturated solution in deuterochloroform did not indicate any significant change in the nature of the hydrogen atom in question. It is thus concluded that an overall aromaticity, and hence structure (IX), is possible.

A consideration of the various bond angles probable in the chelate ring indicates that there will be some deviation from the normal values. This deviation may tend to decrease the stability of any metal complex of the compound relative to what it would be theoretically if the chelate ring were not strained. The size of the metal atom will thus be of great importance for determining not only the amount of overlap between itself and the selenium orbitals, but also between itself and the nitrogen of the pyridyl ring. These two bond strengths will mainly determine the stability of the ring. In the case of Os(IV) the small ionic size (0·67 Å compared to 1·32 Å for Pd^{2+}) probably mitigates against the formation of a ring system.

On the basis of the stabilities of the (dialkyl-M_2)$PtCl_4$ complexes (where M = S, Se, Te) Chatt[8] suggested that the relative co-ordinating affinities of these Group VI atoms for Pt(II) were O < S ⩾ Se < Te. (He was unable to prepare the Se complex in a state pure enough to be used in quantitative studies.) He thus suggests that there will be very little π-bonding between Pt and Se. Pluščec and Westland[17] agree that the π-bond contribution to the platinum–selenium bond is abnormally slight, but state that in the case of L_4PdCl_2 (where L is a monodentate ligand) selenium forms a strong π-bond. They suggest that the order of ligand affinity suggested by Chatt is due to the abnormally weak platinum–selenium bond. From our considerations we suggest that the order for palladium in chelate complexes may well be O < S ⩾ Se > Te.

The contribution by the donor Group VI atom to π-bonding will be governed by the two effects of increase in the size and decrease in the electronegativity of the donor atom. These will be mutually opposed as the atomic number of the atom increases. In the addition compound with 2-(4-pyridyl)benzo[*b*]selenophene, we suggest that these two effects are almost balanced and that a strong Se–Pd π-bond is not possible. Thus the palladium will bond with the other competing ligand atom, (the nitrogen of the pyridyl unit) to give a compound of the structure stated.

In the case of the 2-(2-pyridyl)benzo[*b*]selenophene palladium complex, the delocalization of the electron density around the selenium donor atom by the formation of a π-bond in the then completely conjugated system, increases the apparent electronegativity of the selenium to such an extent that the π-bond is stable.

It is known[18] that in thiophene the screening effect of the 3*d* electrons of the hetero S atom is small, and hence the effective electronegativity of sulphur in thiophene is greater than in the analogous non-aromatic system. By analogy, since the screening effect of the 4*d* electrons of the selenium in 2-(2-pyridyl)benzo[*b*]selenophene is even less than the screening in thiophene, the apparent electronegativity of the selenium will be high. This delocalization will be carried over the ··Se··C··C··N·· system, and hence increase the apparent electronegativity of the selenium. (A similar effect has been used to explain the increased quadrupole resonance frequency of the chlorine in 2-chlorothiophene, due to the decreased σ-bond polarity of the carbon–chlorine bond.[19])

Thus in the conjugated system considered, the probability of π-bonding between the palladium and selenium is high. Further experimental evidence of this π-bonding is obtained by considering the lability of the chlorine atoms in the two complexes, the palladium 2-(2-pyridyl)benzo[*b*]selenophene complex and the 4-pyridyl analogue. In the first, the delocalization of the electron density around the palladium atom should increase the polarity of the palladium–chlorine bond, and hence its strength. This we regard as the reason why the chlorine atoms in this complex may be removed by precipitation with silver only on prolonged boiling, whereas treatment of a warm suspension of the second with silver nitrate results in an immediate precipitate of silver chloride.

We thus conclude that the experimental evidence indicates that, in a suitably arranged chelate system, the grouping ··Se··C··C··N·· is highly selective for palladium, and that delocalization of the electron density by π-bond formation between the palladium and the selenium is a major factor in determining the stability of the chelated complex.

The selectivity of the reagent towards palladium(II) and platinum(II) is determined by two conditions.

(*i*) Only metal ions which have, in the square planar configuration, orbitals available for overlap with the hybrid $4p4d^2$ orbitals of the "aromatic" selenium will be capable of π-bond formation and hence delocalization of the electron density around the central metal atom.

(*ii*) Only such ions that fulfil condition (*i*) and have a size such that there is the minimum deviation from "normal" bond angles when the 5-membered chelate ring containing 4 dissimilar atoms is formed, may form a stable complex.

Of the metals ion species considered, only palladium(II) satisfies both conditions. It is possible that the introduction of groups into the pyridyl system, in such positions as to increase the electron density at the hetero atom will cause greater electron delocalization along the metal to selenium bond and hence give greater stability to the system. If such groups are hydrophobic then it is probable that the solubility of the palladium complex will be sufficiently low to enable the compound to be used as a selective reagent for palladium determinations.

Zusammenfassung—2-(2-Pyridyl)benzo[*b*]selenophen wurde als mögliches Reagens auf Palladium untersucht. Aus einer Betrachtung seiner Reaktionen mit mehreren Metallionen und der wahrscheinlichen Struktur des Komplexes aus der Verbindung und Palladium wird geschlossen, daß die Gruppe —Se⋯C⋯C⋯N— hochselektiv für Palladium sein kann. Nach den experimentellen Ergebnissen wird vermutet, daß die Delokalisierung der Elektronendichte an den Metallatomen durch Bildung von π-Bindungen zwischen Palladium- und Selenatom ein wesentlicher Faktor bei der Stabilisierung des Chelates ist.

Résumé—On a étudié la 2-(2-pyridyl) benzo [*b*] sélénophénone en tant que réactif possible du palladium. En considérent ses réctions avec divers ions métalliques et la structure probable du complexe formé entre le composé et le palladium(II), on admet que le groupe —Se⋯C⋯C⋯N— peut être hautement sélectif du palladium. En se basant sur l'expérience, on suggère que la délocalisation de la densité électronique du métal par formation de liaison π entre les atomes de palladium et de sélénium est un facteur essentiel dans la détermination de 'a stabilité du complex chélaté.

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KINETICS OF THE PRECIPITATION OF PALLADIUM DIMETHYLGLYOXIMATE FROM HOMOGENEOUS SOLUTION

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Summary—The kinetics of formation of palladium dimethylglyoximate in the post-nucleation and pre-nucleation stages, and the effect of palladium on the reaction of biacetyl and hydroxylamine, have been studied.

PALLADIUM[1] and nickel[2] have been precipitated with dimethylglyoxime from homogeneous solution by the reaction of biacetyl and hydroxylamine. The kinetics and mechanism of the precipitation of nickel have been investigated by Hileman and Gordon.[3] A preliminary study of the kinetics and mechanism of the reaction of biacetyl and hydroxylamine in the absence of palladium has been carried out by Ellefsen and Gordon.[4] A study of the effect of palladium on this reaction sequence and a study of the kinetics of formation of palladium dimethylglyoximate in the pre-nucleation and post-nucleation stages are presented in this paper.

EXPERIMENTAL

Apparatus

All spectrophotometric measurements were carried out on a Cary Model 14 spectrophotometer equipped with a cell compartment thermostatically controlled to 0·05°.

Reagents

Hydroxylamine hydrochloride, biacetyl monoxime, biacetyl and dimethylglyoxime were prepared as described previously.[3]

Palladium chloride (J. T. Baker) was dissolved in very dilute hydrochloric acid and its concentration was determined by precipitation with dimethylglyoxime.

Procedures

In the pre-nucleation experiments, a spectrophotometric cell containing known concentrations of hydrochloric acid, hydroxylamine hydrochloride and palladium was brought to constant temperature. A known amount of biacetyl monoxime in solution was then added by means of a Hamilton microlitre syringe (0·0500-ml capacity) fitted with a Chaney adaptor. The absorbance was measured as a function of time, at 3800 Å where a minimum occurs in the spectrum of the palladium chloride complex (*cf.* Fig. 1).

In the post-nucleation experiments, gravimetric analysis was used. Several identical solutions containing hydroxylamine hydrochloride, hydrochloric acid and palladium were brought to constant temperature and a solution of biacetyl monoxime was added to each by pipette. At various times after the formation of palladium dimethylglyoximate, the solid phase was removed, dried and weighed.

RESULTS AND DISCUSSION

Abbreviations

B = biacetyl
HM = biacetyl monoxime

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HD = dimethylglyoxime
Hx = hydroxylamine
PdD_2 = palladium dimethylglyoximate
$PdCl_4^{2-}$ = palladium chloride complex
A = absorbance
$[X]_i$ = initial concentration of species X in mole.l.$^{-1}$
k_2' = rate constant for the reaction of biacetyl monoxime with hydroxylamine
ϵ = molar absorptivity

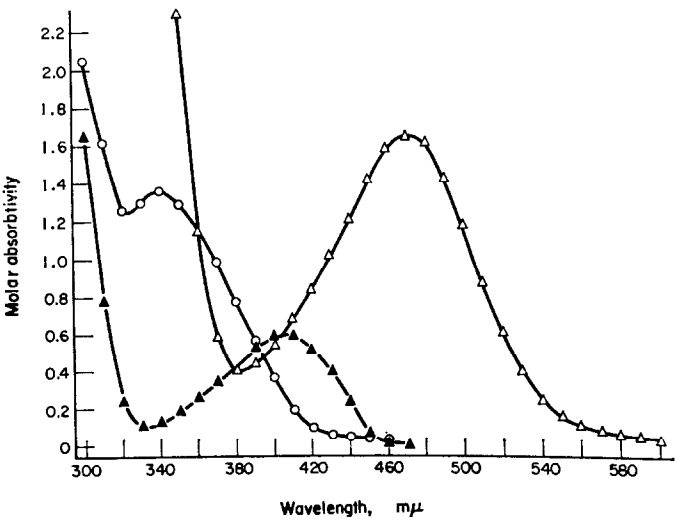

FIG. 1.—The visible spectra of biacetyl, palladium chloride complex and palladium dimethylglyoximate at 25·0°C in 2·00*M* KCl and 0·406*M* HCl.
▲—Biacetyl, × 10^{-1}
△—Palladium chloride, × 10^{-2}
○—Palladium dimethylglyoximate, × 10^{-3}.

Reactions of the palladium chloride complex

The visible spectra of biacetyl, the palladium chloride complex and palladium dimethylglyoximate are shown in Fig. 1. Dimethylglyoxime and biacetyl monoxime do not absorb in the visible region. The spectrum of palladium dimethylglyoximate is less exact than the other two spectra owing to the larger errors involved in measuring the absorbance of the very sparingly soluble chelate. The absorbance of a nearly saturated solution of palladium dimethylglyoximate was measured in a 10-cm cell used in conjunction with a slide wire giving full-scale expansion for the range 0·0–0·1.

Biacetyl monoxime reacted rapidly with the palladium chloride complex in neutral solution producing a yellow complex with the spectrum shown in Fig. 2. The complex slowly underwent some further unknown reaction; the absorbance in the visible region gradually decreased with no new peaks appearing.

A very slow reaction occurs in a solution (at 25°) in which [HM] = $4{\cdot}64 \times 10^{-3}M$, [B]* = $0{\cdot}115M$, $[PdCl_4^{2-}] = 9{\cdot}39 \times 10^{-4}M$ and [HCl] = $0{\cdot}406M$. The absorbance at 4800 Å (*cf.* the maximum in the spectrum of the palladium chloride complex in

* Biacetyl monoxime decomposes in acid solution. With biacetyl present virtually none of the monoxime decomposes.[4]

Fig. 1) decreased by about 5% in 7 hr. If the reaction mixture is also made 2·00*M* in potassium chloride, the absorbance remains virtually constant for 19 hr. Obviously, neither biacetyl nor biacetyl monoxime forms complexes with palladium to a detectable extent under these conditions. The lack of reaction can be attributed to both hydrogen and chloride ions, *i.e.*, biacetyl monoxime is converted into its unreactive un-ionized species and at the same time the dissociation of the palladium chloride complex is

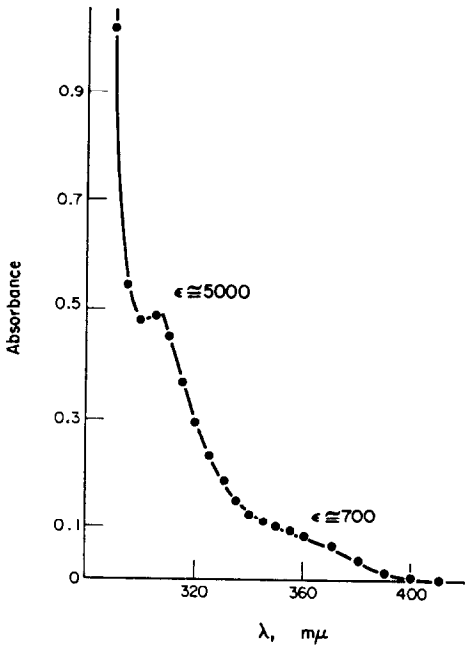

FIG. 2.—Spectrum of the biacetyl monoxime–palladium complex.

suppressed. In a similar manner, it was found that palladium would not react with hydroxylamine under these conditions, this being attributable to the formation of unreactive protonated hydroxylamine[5] and to the stability of the palladium chloride complex.

All subsequent reactions were carried out at 25° in 2·00*M* potassium chloride and 0·406 or 0·203*M* hydrochloric acid. This was done because it was found that the generation of dimethylglyoxime from biacetyl (or biacetyl monoxime) and hydroxylamine is essentially unaffected by the presence of palladium, greatly simplifying the kinetics. Biacetyl monoxime is stable in acid solution in the presence of excess of hydroxylamine hydrochloride[4] and initiation of the reaction sequence with biacetyl monoxime instead of biacetyl introduced an additional simplification.

Pre-nucleation kinetics

The mechanism for the formation of palladium dimethyglyoximate in the pre-nucleation stage has been found to be the following:

$$HM + Hx \xrightarrow{k_2'} HD + H_2O \quad (1)$$

$$HD + PdCl_4^{2-} \xrightarrow{k_3} PdDCl_2^- + 2Cl^- + H^+ \quad (2)$$

$$HD + PdDCl_2^- \xrightarrow{k_4} PdD_2 + 2Cl^- + H^+. \quad (3)$$

The formation of dimethylglyoxime is shown in equation (1) by a simplified mechanism.[4] As shown by equation (2), some intermediate such as $PdDCl_2^-$ is formed, but its exact nature has not been determined.

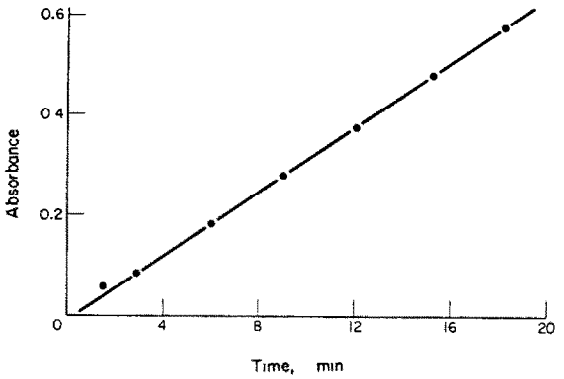

FIG. 3.—Rate of formation of PdD_2 at 25·0°C, from absorbance measurements at 3800 Å.
[KCl] 2·00M; [HCl] 0·406M; $[Hx]_i$ 3·714 × $10^{-2}M$; $[HM]_i$ 2·092 × $10^{-3}M$; $[Pd]_i$ 2·359 × $10^{-3}M$.

The reaction of high concentrations of biacetyl monoxime and hydroxylamine in the presence of palladium resulted in a linear increase in absorbance at 3800 Å over a period of 20 min (Fig. 3). A decrease in the concentration of biacetyl monoxime

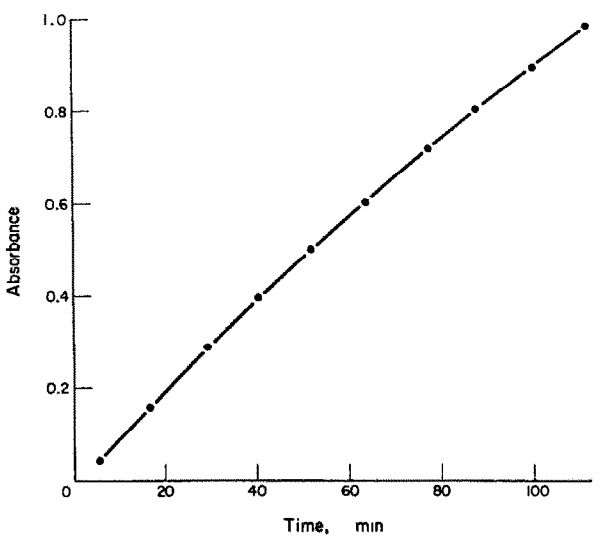

FIG. 4.—Rate of formation of PdD_2 at 25·0°C, from absorbance measurements at 3800 Å.
$[HM]_i$ 6·973 × $10^{-4}M$; other conditions as for Fig. 3.

resulted in the curved line shown in Fig. 4. A precipitate was not obtained in either of these experiments despite the very high supersaturations of palladium dimethylglyoximate existing towards the end of the reaction periods.

Preliminary investigations showed it could be assumed that (*a*) the increase in

absorbance is due to the formation of palladium dimethylglyoximate, (*b*) the concentration of the intermediate species $PdDCl_2^-$ is negligibly small ($k_4 \gg k_3$), (*c*) the formation of dimethylglyoxime by equation (1) is the rate determining step, (*d*) the presence of palladium has no significant effect on the generation of dimethylglyoxime, and (*e*) all the reactions are essentially irreversible. Then the rate constant k_2' and the molar absorptivity of palladium dimethylglyoximate at 3800 Å can be determined as shown in the following discussion.

The concentrations of HM and Hx given in Fig. 3 are high enough for the reaction to be pseudo zero-order. Thus,

$$\frac{d[PdD_2]}{dt} = \frac{k_2'[HM][Hx]}{2} = k_2'' \tag{4}$$

$$[PdD_2] = k_2'' t \tag{5}$$

$$A_{PdD_2} = k_2'' \epsilon_{PdD_2} t. \tag{6}$$

The value of $k_2''\epsilon_{PdD_2}$ and hence of $k_2'\epsilon_{PdD_2}$ can be obtained from the slope of the line in Fig. 3.

The concentration of HM given in Fig. 4 is smaller and the reaction is pseudo first-order. Hence

$$\ln\left\{\frac{[HM]_1}{[HM]_1 - 2A_{PdD_2}/\epsilon_{PdD_2}}\right\} = k_2'[Hx]t. \tag{7}$$

Because the value of $k_2'\epsilon_{PdD_2}$ is known, equation (7) can be solved for k_2' and ϵ_{PdD_2}.

By this method, the values obtained are $k_2' = 0{\cdot}115$ l.mole^{-1}.min^{-1} and $\epsilon_{PdD_2} = 770$; the value of ϵ_{PdD_2} has been corrected for the slight decrease in absorbance resulting from the disappearance of the palladium chloride complex.

The value of k_2' agrees quite well with the value of 0·0954 l.mole^{-1}.min^{-1} obtained by Ellefsen and Gordon[4] under essentially the same conditions except for the absence of palladium and with a somewhat higher concentration of hydroxylamine hydrochloride.

The value of ϵ_{PdD_2} obtained by the kinetic method agrees favourably with an approximate value obtained from the absorbance of a nearly saturated solution of palladium dimethylglyoximate of known concentration. At 3800 Å, the value of ϵ_{PdD_2} obtained was 816 ± 50. The results indicate that the assumptions made are justifiable.

In Fig. 5, the results are shown for the reaction of a large concentration of biacetyl monoxime and hydroxylamine in the presence of a variable amount of palladium. The generation of dimethylglyoxime is a pseudo zero-order reaction, and in each case the concentration of palladium is sufficiently high to be considered constant over the time-span used. As the concentration of palladium is decreased, an increasing period of time elapses before the increase in absorbance with time becomes linear (and the same in all cases). This is attributed to the time required for the build-up of a steady-state concentration of dimethylglyoxime and $PdDCl_2^-$. Some intermediate such as $PdDCl_2^-$ must be present because it is unlikely that PdD_2 would be formed by a three-body collision.

The concentrations of palladium in all experiments were high enough for reaction

(2) to be considered pseudo first-order. At higher concentrations of palladium such as in Figs. 3 and 4, the steady-state concentration of dimethylglyoxime is lower than that at the lower concentrations of palladium shown in Fig. 5. The concentration of $PdDCl_2^-$ is low in all cases. Therefore, the time required for generation of the steady-state concentrations of these species is less at higher concentrations of palladium than at lower. The curves shown in Figs. 3 and 4 can almost be extrapolated back to zero in contrast to the curves at the lower concentrations of palladium in Fig. 5.

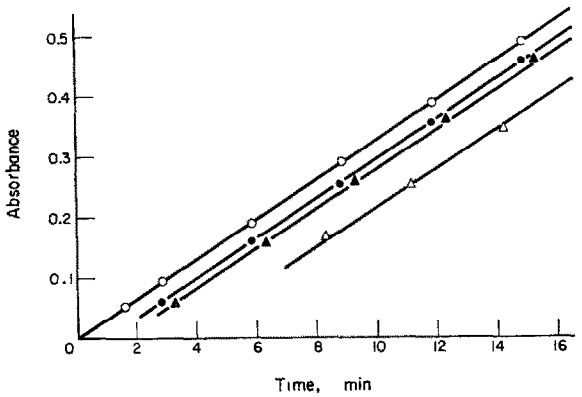

FIG. 5.—Effect of the initial palladium concentration on the rate of formation of PdD_2 at 25°C.
$[Pd]_i$: ○—$2{\cdot}359 \times 10^{-3}M$; ●—$1{\cdot}769 \times 10^{-3}M$; ▲—$9{\cdot}436 \times 10^{-4}M$; △— $3{\cdot}539 \times 10^{-4}M$; other conditions as for Fig. 3.

Post-nucleation kinetics

The rate constant k_2' was determined in the post-nucleation stage from the amount of palladium dimethylglyoximate precipitated. The amounts of biacetyl monoxime and hydroxylamine consumed by the reaction were calculated from the quantity of dimethylglyoxime in the precipitate. This determination of the rate constant makes use of the assumptions mentioned in the section on pre-nucleation kinetics; the further assumption is made that all the dimethylglyoxime formed is present as palladium dimethylglyoximate. Other experiments in which palladium was precipitated from $2{\cdot}00M$ potassium chloride solution indicated no detectable increase in its solubility in this medium. The results obtained in the determination of k_2' are shown in Table I.

It can be seen that the observed rate constant increases with time, eventually reaching a limiting value. The low values obtained during the initial stages of the reaction indicate that supersaturation has not yet been relieved. The crystal growth step is not fast compared to reaction (1) until the rate of generation of palladium dimethylglyoximate decreases appreciably and until larger quantities of palladium dimethylglyoximate are present to offer many growth sites. At this stage, supersaturation approaches zero and the rate of formation of the solid phase is no longer a surface controlled reaction.

The limiting value of k_2' obtained in $0{\cdot}406M$ hydrochloric acid is about 0·127 $l.mole^{-1}.min^{-1}$. This is slightly higher than the value of 0·115 $l.mole^{-1}.min^{-1}$ obtained in the pre-nucleation stage. In $0{\cdot}203M$ acid, the limiting value of k_2' obtained is about 0·138 $l.mole^{-1}.min^{-1}$.

It is to be noted here that in both the post-nucleation, and pre-nucleation stages the rate constant is not a function of the initial concentrations of biacetyl monoxime, hydroxylamine or palladium.

TABLE I.—GRAVIMETRIC DETERMINATION OF k_3' IN THE POST-NUCLEATION STAGE IN 2·00M POTASSIUM CHLORIDE AT 25·0°C

$[Hx]_i$ $M \times 10^2$	$[HM]_i$ $M \times 10^3$	$[Pd]_i$ $M \times 10^4$	[HCl] M	Reaction time, *min*	Pd found, *mg*	k_3' $l.mole^{-1}.min^{-1}$
3·714*	1·857*	9·386*	0·406	43·1	3·01	0·0813
				109·9	9·75	0·124
				175·1	13·84	0·128
3·714	1·857	14·08	0·406	38·3	3·29	0·100
				57·6	5·10	0·108
				111·2	9·79	0·123
				182·4	14·16	0·127
				233·1	16·31	0·127
				293·3	18·15	0·124
3·714	1·857	28·16	0·203	29·8	1·11	0·0413
				65·2	4·37	0·0805
				109·5	8·36	0·102
				173·4	12·98	0·117
				229·3	16·34	0·129
				297·7	19·79	0·147
3·714	1·857	9·386	0·203	145·4	13·02	0·140
				249·0	17·77	0·140
				312·1	19·54	0·138
3·714	1·393	9·386	0·203	164·4	10·55	0·139
				276·0	13·97	0·138
				401·5	16·06	0·137
3·714	2·321	9·386	0·203	76·9	10·10	0·140
				146·7	15·45	0·129
				200·9	19·60	0·138
7·429	1·857	9·386	0·203	43·1	8·73	0·137
				83·8	14·19	0·138
				130·9	18·11	0·137

* *i.e.*, 0·03714M; 0·001857M, and 0·0009386M respectively.

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Zussammenfassung—Die Kinetik der Bildung von Palladiumdimethylglyoximat in den Stadien nach und vor der Keimbildung und der Einfluß von Palladium auf die Reaktion zwischen Biacetyl und Hydroxylamin wurden untersucht.

Résumé—On a étudié les cinétiques de formation du diméthylglyoximate de palladium aux stades de post- et pré-amorçage, ainsi que l'influence du palladium sur la réaction du biacétyle et de l'hydroxylamine.

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MASS SPECTROMETRY OF METAL CHELATES—I

DETECTION ON THE PICOGRAM SCALE

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Summary—A method has been developed for the detection and estimation of metals in the form of chelates in amounts down to 10^{-12} g. The chelate is evaporated into the source of a mass spectrometer and a continuous record of the ion current at a significant mass number is made. The integrated ion current is directly proportional to the concentration of metal chelate.

VERY small quantities of impurities in metals are commonly estimated with the aid of a spark source mass spectrometer. With this instrument a sample of the metal is vaporized before ionization and the ion currents corresponding to the components of the metal mixture are recorded on a photographic plate. The limit of detection of impurities in a sample is set at one part in 10^9. The chelates of many metals vaporize at temperatures considerably lower than those at which the parent metals have a detectable vapour pressure. As a result, it is possible to detect such metals as their chelates in the source of a conventional mass spectrometer such as the A.E.I. M.S.9 at temperatures between about 200° and 500°. It is the purpose of the present paper to describe a method in which the integrated ion current at a particular *m/e* value may be related to the concentration of a metal chelate and hence of the metal.

EXPERIMENTAL

Apparatus

All measurements were made with an A.E.I. M.S.9 mass spectrometer fitted with an insertion lock and a direct evaporation probe. Samples were admitted in pyrex glass tubes 27 mm long and 1 mm internal diameter which were fitted to the end of the probe and thrown away after use. The tubes were filled with up to 5 μl of the metal chelate solution by means of a Hamilton syringe (701-NW/G).

Reagents

Nickel dimethylglyoximate was supplied by Dr. W. I. Stephen. The sample was recrystallized from dimethylsulphoxide.

Nickel benzildioximate was obtained from the same source.

Heptacosafluoro-tri-n-butylamine was supplied by Koch–Light Laboratories Ltd.

A stock solution of nickel dimethylglyoximate was made by dissolving 1·00 mg in 10 ml of chloroform. It was stored cold.

Procedure

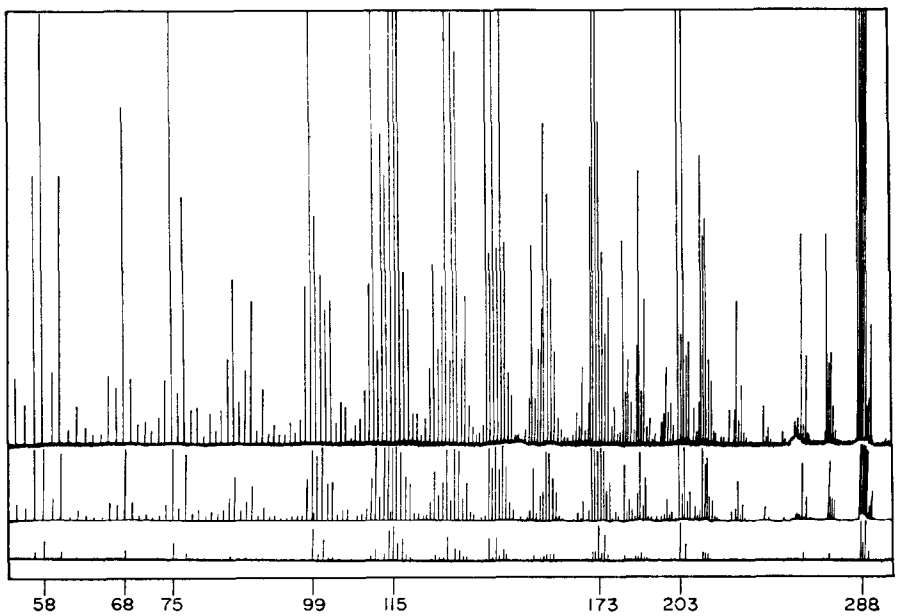
A measured volume (1–5 μl) of a solution of nickel dimethylglyoximate in chloroform was injected into the sample tube, which was then transferred to the vacuum system of the mass spectrometer through the insertion lock, and held in the cool part of the system. A measured pressure of heptacosafluoro-tri-n-butylamine was admitted to the gas-inlet system. The peak at *m/e* = 219 ($C_4F_9^+$) was selected and displayed on the oscilloscope. The decadic resistance was then set to a value of 1·315351 (the mass ratio for $C_8H_{14}N_4O_4Ni^+/C_4F_9^+$) and the peak switching system so adjusted that the oscilloscope gave an alternate display of the mass peaks at 219 and 288 ($C_8H_{14}N_4O_4Ni^+$). At this stage, the peak at *m/e* = 288 should not appear. The galvanometer recorder was then set in operation,

so as to record only the peak pair displayed on the oscilloscope. The sample tube was then lowered into the heated region of the source (*ca.* 250°) to allow evaporation of the metal chelate. When evaporation begins the peak at $m/e = 288$ appears on the oscilloscope and is recorded. Evaporation is complete in 10–20 sec depending on sample size, and the peak at $m/e = 288$ then disappears from the oscilloscope and the recorder trace. The amount of metal chelate evaporated is proportional to the integrated ion current at $m/e = 288$, and therefore to the area under the envelope of the $m/e = 288$ peaks on the recorder trace.

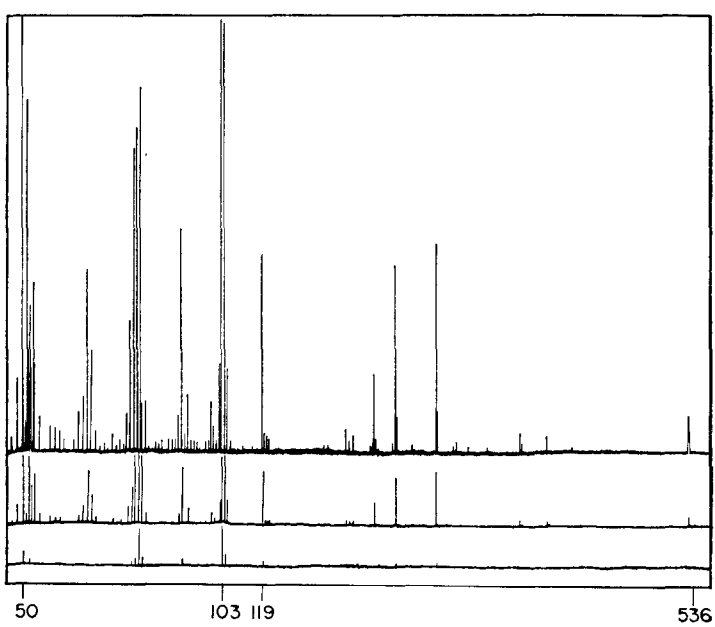
RESULTS AND DISCUSSION

It has been common practice, when carrying out quantitative analysis with a mass spectrometer, to provide a reservoir of sample vapour, the pressure of which remains substantially constant while a mass spectrum is recorded. The partial pressure of a component in the sample is then proportional to the height of mass peaks on the recorder trace which are due to that component only. The proportionality constant or sensitivity for each peak is determined by recording separately the mass spectrum of the pure component at a known pressure. The low volatility of metal chelates and the need to estimate minute quantities militates against the use of this procedure. Indeed, the only satisfactory method of recording the mass spectra of metal chelates is by their direct evaporation into the ion source from a probe which can be inserted into the vacuum system of the mass spectrometer. When such a device is used, however, two problems arise. The partial pressure of the metal chelate changes during the time required to record a mass spectrum, so that it is no longer possible to apply previously determined sensitivities, and in addition, at very low concentrations of the metal chelates, evaporation may be complete before the mass spectrum has been recorded. There is a further instrumental complication, in that the sensitivity of the instrument itself may change owing to deliberate or unintentional variations in the gain of the electron multiplier. It is therefore necessary to provide an internal standard of which the partial pressure is known and remains constant, and of which the mass spectrum may be recorded at the same time as that of the metal chelate. This may be most simply achieved by providing a reservoir of the vapour of heptacosa-fluoro-tri-n-butylamine (a compound commonly used as a mass marker in mass spectrometry) at a known pressure and allowing this to leak into the ion source at a constant rate at the same time as the metal chelate is evaporating.

As the complete mass spectrum of the metal chelate at low concentration cannot be recorded in the evaporation time, and because even if this were possible the mass peak sensitivities would not remain constant, it was decided to use a single mass peak characteristic of the metal chelate and to record the rise and fall of the ion current at this particular mass value during the course of the evaporation. The integrated ion current would then be directly proportional to the amount of metal chelate evaporated, and hence to the concentration of metal in the original sample, provided that no irreproducible thermal breakdown occurs during evaporation. The most suitable ion for this purpose would be that most characteristic of the metal chelate, and hence the molecule ion itself would be most desirable. Not all molecules exhibit a mass spectrum in which the molecule ion is represented by a mass peak, because some molecule ions are unstable. For this reason, two simple, moderately volatile, easily available chelates of nickel, the dimethylglyoximate and benzildioximate compounds, were obtained and their mass spectra recorded. In these preliminary experiments, solid samples were used in order to maintain an approximately constant rate of evaporation. The results shown in Fig. 1(a) and (b) reveal that the molecule ions of the two chelates were



(a) Nickel dimethylglyoximate



(b) Nickel benzildioximate

FIG. 1.—Mass spectra of nickel chelates

sufficiently stable to provide large mass peaks in the spectrum. The peak at $m/e = 288$ corresponding to the ion $C_8H_{14}N_4O_4{}^{58}Ni^+$ was selected from the spectrum of nickel dimethylglyoximate as suitable for quantitative studies, the rise and fall of this peak and the integrated ion current being recorded. There is an instrumental difficulty associated with such a recording in that no mass spectrometer can provide a means of tuning in the ion current at a selected m/e value before the ion current itself has been established. Thus, a method had to be found in which the instrument could record the ion current at $m/e = 288$ before, during and after evaporation. The method employed was to use a second substance, in this case heptacosafluoro-tri-n-butylamine, which did not exhibit a spectrum containing a peak at $m/e = 288$. A constant partial pressure of this substance is maintained within the ion source, using the conventional gas handling facilities of the instrument. It is then possible to select a peak from the mass spectrum of this compound which is close to $m/e = 288$. The peak selected is then displayed on the oscilloscope facilities of the instrument by the normal tuning in procedure. Using the peak comparison technique, it is now possible to display on the oscilloscope alternately the reference peak, which in this case is $m/e = 219$ ($C_4F_9^+$), and that at $m/e = 288$. This is achieved on the model M.S.9 by adjusting the decadic resistance to a value given by the ratio of the precise masses of the ions responsible for the peaks at m/e 219 and 288.

$$\frac{288{\cdot}055269}{218{\cdot}985620} = 1{\cdot}315407$$

A recorder trace taken at this stage shows only the $m/e = 219$ peak repeated at intervals see [Fig. (2a)]. When the sample is lowered into the heating region of the ion source, and evaporation begins, a second peak appears between the repeated $m/e = 219$ peaks. In sharp distinction from the latter, which has a constant height, this second peak ($m/e = 288$) increases in height, reaches a maximum and then decays and finally disappears. It is the envelope of these secondary peaks [see Fig. (2b)] which is a record of the rise and fall of the ion current at $m/e = 288$, and it is therefore the area under this envelope which is proportional to the integrated ion current and hence to the concentration of metal chelates.

It can now be seen that the reference compound serves a two-fold purpose, it enables the mass scale to be calibrated so that the rise and fall of the selected sample peak can be completely recorded and it provides an internal standard against which any variation of instrument sensitivity may be measured.

The alternative procedure of recording continuously the peak height at $m/e = 288$ was discarded because instrumental drift caused the peak height to vary during evaporation. The peak comparison technique, although providing an interrupted rather than a continuous trace, ensured that the full peak height was always recorded.

The ultimate sensitivity of the instrument using this technique was now investigated. The stock solution of 0·01 % nickel dimethylglyoximate in chloroform was successively diluted by factors of 10, and 1 μl of the solution was examined at each dilution. The sensitivity of the instrument itself could be varied over several orders of magnitude by adjustment of the electron multiplier gain and the electron beam current. Figure 2(b) shows the recorder trace obtained from 1 μl of the stock 0·01 % solution, corresponding to a total sample weight of 10^{-7} g. This was recorded at low sensitivity, and the sample size could be reduced to 10^{-10} g before it was necessary to increase the

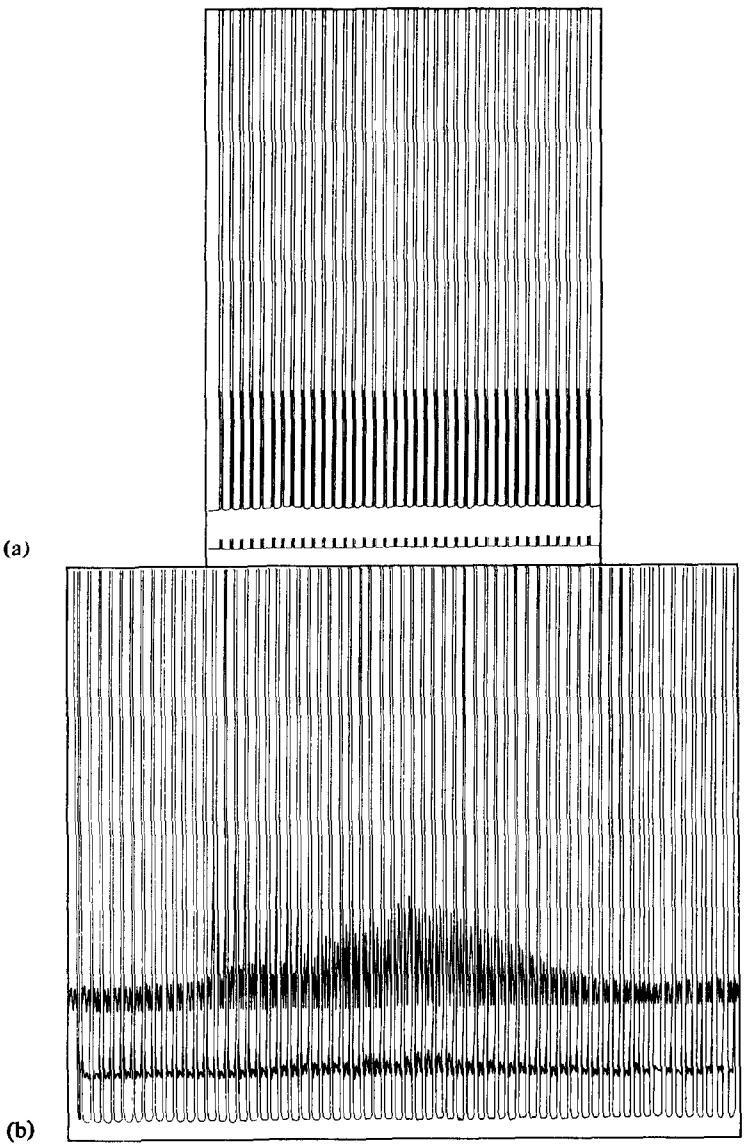


FIG. 2.—Continuous records of peaks at *m/e* 219 and 288.
(a) Before evaporation of nickel dimethylglyoximate
(b) During evaporation.

electron multiplier gain. As the gain was increased the signal-to-noise ratio was reduced, but at the highest usable gain the sample size could be reduced to 10^{-14} g (see Fig. 3).

With the electron multiplier gain constant, a series of determinations were made for different sample sizes. When the area under the envelope is plotted against sample size a straight-line relationship is obtained.

When determinations were repeated with stock solutions which had been allowed to stand for a day, it was found that the sensitivity had apparently dropped. This effect was traced to the instability of nickel dimethylglyoximate in chloroform, by the

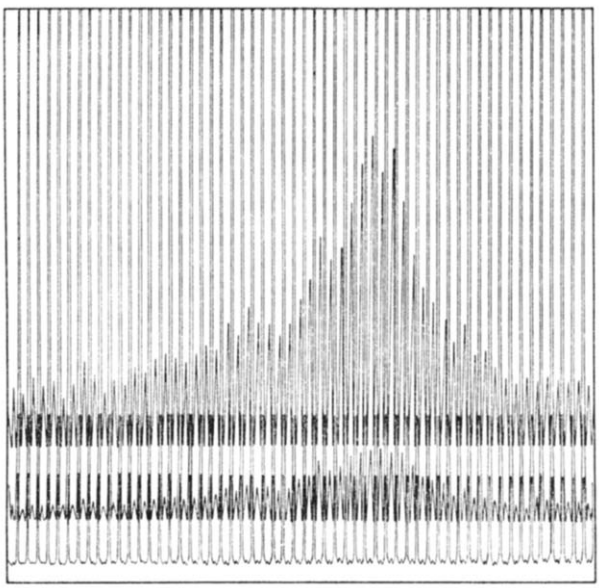


FIG. 3.—Record obtained during evaporation of 10^{-14} g of nickel dimethylglyoximate.

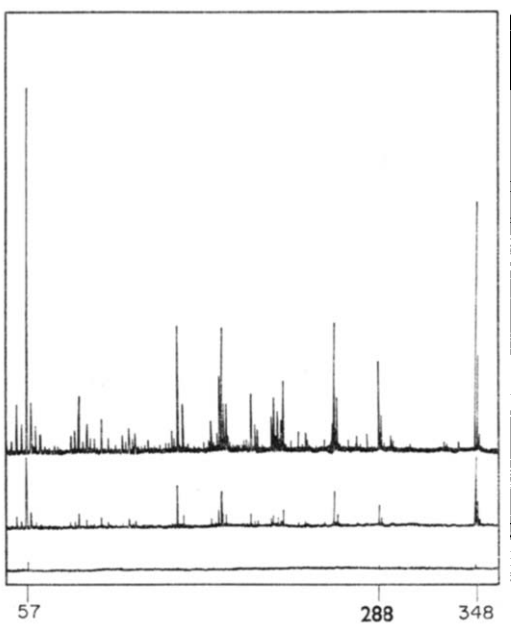


FIG. 4.—Mass spectrum of decomposition products of nickel dimethylglyoximate in chloroform.

observation of the appearance of a small subsidiary peak at $m/e = 288$, due to an ion with a mass sufficiently different from that of $C_8H_{14}N_4O_4{}^{58}Ni^+$ to be resolved by the instrument at low resolution. The determination of its precise mass revealed that it contained no nickel.

A complete mass spectrum was therefore recorded for the stock solution at various times after its preparation. This spectrum is illustrated in Fig. 4 and reveals the gradual

decay of the nickel dimethylglyoximate molecule ion peak, and the rise of peaks at m/e values above 288. Precise mass measurements of these peaks revealed that the corresponding ions contained no nickel atoms. The compounds responsible for these spectra are most probably formed by the polymerization of dimethylglyoxime molecules or their breakdown products. It can be demonstrated that several compounds are involved, by recording a mass spectrum very rapidly (8 sec) as soon as the sample is lowered into the heating region of the source, and before evaporation of the chelate has begun. Such a spectrum contains no peaks due to ions containing nickel atoms, and must be derived from a compound more volatile than the metal chelate. However, the spectrum obtained from the chloroform solution on prolonged standing does not correspond to a simple superposition of this spectrum on that of the metal chelate.

CONCLUSIONS

A method has been devised for the detection of metal chelates in quantities down to 10^{-14} g. Quantitative determination of these low concentrations is dependent on the development of an unequivocal procedure for calibrating the instrument. It has been found that because of their instability the stepwise dilution of chloroform solutions of nickel dimethylglyoximate does not provide a reliable calibration procedure unless the solutions are used immediately.

Acknowledgement—The authors wish to thank Miss M. Reade for her assistance in recording the mass spectra.

Zusammenfassung—Eine Methode zu Nachweis und Bestimmung von Metallen in Form von Chelaten in Mengen bis herunter zu 10^{-13} g wurde entwickelt. Das Chelat wird in der Ionenquelle eines Massenspektrometers verdampft und der Ionenstrom bei einer geeigneten Massenzahl registriert. Der integrierte Ionenstrom ist direkt proportional zur Chelatkonzentration.

Résumé—On a élaboré une methode pour la détection et l'estimation de métaux sous forme de chélates en quantités pouvant descendre jusqu'à 10^{-12} g. On évapore le chélate dans la source d'un spectromètre de masse et effectue un enregistrement continu du courant ionique à un nombre de masse significatif. Le courant ionique intégré est directement proportionnel à la concentration du chélate métallique

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ANION-EXCHANGE SEPARATION OF COBALT FROM NICKEL

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Summary—An anion-exchange method has been developed for the separation of cobalt from nickel, based on the observation that from a malonic acid solution containing sodium nitrite, cobalt is preferentially adsorbed by the exchanger but nickel passes through. The cobalt is eluted with 2*M* ammonium chloride in dilute ammonia solution. From an ammonium malonate solution containing chloride and nitrate, cobalt is quantitatively electro-deposited on a platinum cathode to give a bright, adherent deposit. Nickel is deposited from a solution of similar composition.

AMONG the available methods for the determination of cobalt, the titrimetric procedure with EDTA,[1] and the two gravimetric procedures[1] based on precipitation with 1-nitroso-2-naphthol and on electro-deposition appear to be the most popular. While the first two procedures cannot handle more than 50 mg of cobalt, the electrogravimetric procedure is more flexible, enabling much higher quantities to be determined. The 1-nitroso-2-naphthol method suffers from the fact that the oxygen–cobalt ratio in the final weighing form Co_3O_4 is not strictly stoichiometric. The more accurate electro-gravimetric procedure is also not entirely satisfactory. Salyer and Sweet[2] have critically examined the different electrolytic baths proposed and shown that slightly higher results are obtained in every case although cobalt in amounts varying from 0·05 to 4 mg remains in solution. Depending on the depolarizers added to the bath, the cobalt deposits are contaminated with carbon, sulphur or phosphorus.

When cobalt and nickel co-exist, they have to be separated from one another before the titrimetric or electrolytic methods can be employed. Most of the methods of separation of cobalt from nickel are based on[3,4,5] the selective adsorption from hydrochloric acid solution of the chloro-complex of cobalt on a strongly basic anion-exchanger. A recent report indicates that an anion-exchange separation is also possible by preferentially adsorbing cobalt from a cyanate solution.[6]

While investigating the complex formation of some transition metals with malonic acid and its derivatives, we have observed that both cobalt and nickel give bright adherent quantitative deposits on a platinum cathode from a malonic acid bath. Cobalt is also quantitatively taken up on a strongly basic anion-exchanger to the exclusion of nickel from a malonic acid solution containing nitrite. The methods developed, based on these observations, for the separation of cobalt from nickel and its electro-deposition, are reported in this communication.

EXPERIMENTAL

A conventional type of electro-analysis assembly was used. The cathode was a hollow perforated platinum cylinder (surface area about 35 cm^2) and the anode a stout platinum wire, coiled into a helix

and suspended at the centre of the cathode. A Bausch and Lomb Spectronic 20 was used for colorimetric estimation.

Beds, 15 × 2 cm, of Amberlite IRA 400, −80 + 200 BSS, 8% cross linked chloride form, were used for the anion-exchange.

Reagents

Malonic acid prepared by the Fine Chemicals Section of this laboratory was used. All other chemicals were of AnalaR grade. The eluting agent for cobalt was 2*M* ammonium chloride in dilute ammonium hydroxide.

Electro-deposition

The volume of the electrolytic bath was maintained at around 150 ml. Electrolysis was carried out at room temperature. Completeness of electro-decomposition of cobalt was tested for by treating a few drops of the electrolyte with 0·5% aqueous nitroso-R-salt solution after buffering with 50% aqueous sodium acetate and acidifying with nitric acid. Nickel was tested for with dimethylglyoxime.

After deposition the cathode was rinsed with water and ethanol, dried at 100°, cooled and weighed. The cobalt deposit was dissolved in cold concentrated nitric acid, fumed with sulphuric acid, heated to 600° in a platinum dish, cooled and weighed as cobalt sulphate.

Anion-exchange separation of cobalt from nickel

Solutions of cobalt and nickel chlorides were prepared from their pure salts and standardized. Cobalt was determined as sulphate (after 1-nitroso-2-naphthol precipitation) and nickel by precipitation with dimethylglyoxime. The anion-exchange resin was poured in the form of a slurry into a Pyrex glass column and converted into the chloride form with hydrochloric acid.

The desired volumes of standard cobalt and nickel solutions were mixed in a 250-ml beaker; 2 g of malonic acid were added and the solution was diluted to about 100 ml and warmed. Then 2 g of sodium nitrite dissolved in 15 ml of water were added slowly to the solution, which was then cooled to room temperature and passed through the anion-exchanger at the rate of 5 ml/min. The column was flushed with 60 ml of 1% ammonium chloride solution. The effluent then contained all the nickel, while the column held the cobalt in the form of an anionic-complex. The nickel in the effluent was determined either by precipitation with dimethylglyoxime or by electro-deposition from a malonic acid medium. The bromine-dimethylglyoxime colorimetric method was used for amounts of nickel below 5 mg.

The cobalt was eluted with 2*M* ammonium chloride in dilute ammonia solution at the rate of 5 ml/min, 80–100 ml of the eluent sufficing for complete elution of cobalt. Because of the intense red colour of the adsorbed cobalt band, its movement down the column was readily followed. The effluent containing the cobalt was acidified with hydrochloric acid, boiled to remove nitrous fumes, and cooled. To the cooled solution, 4 g of malonic acid, 3 g of ammonium nitrate and 30 ml of dilute ammonia solution (1 + 1) were added, the mixture was diluted to 150 ml, and the cobalt was determined by electro-deposition. Cobalt in amounts less than 2 mg was determined by the colorimetric nitroso-R-salt method.

RESULTS AND DISCUSSION

Electro-deposition of cobalt

From an ammonium malonate bath containing chloride or sulphate, cobalt was deposited on the perforated platinum cathode almost quantitatively, but the deposit was dull and non-adherent. Curiously enough, when to such a bath a little ammonium nitrate (which ordinarily inhibits[7] the deposition of cobalt) is added, the cathodic deposit is bright, adherent and quantitative. However, increasing amounts of nitrate prolong the time needed for deposition. For instance, complete deposition of 200 mg of cobalt takes over 150 min when 10 g of ammonium nitrate are added to the bath, but if the initial concentration of the nitrate is controlled, quantitative deposition is effected in a reasonable time. The deposition of nickel from such baths also proceeds satisfactorily. Table I shows typical results for the deposition of cobalt and nickel from malonate baths. Deposition of over 1 g of cobalt is complete in about 90 min at a current of 9 A/dm^2. The desirable physical characteristics of the deposit are

TABLE I.—ELECTRO-DEPOSITION OF COBALT AND NICKEL FROM A MALONIC ACID BATH

No.	Co taken *mg*	Cathode deposit of Co, *mg*	Cobalt weighed as $CoSO_4$, *mg*
1	5·6	5·5, 5·3, 5·3	—
2	34·8	35·0	92·2 (92·0)*
3	56·0	56·1	147·4 (147·6)
4	87·1	87·1	229·4 (229·2)
5	268·0	267·5	703·8 (705·0)
6	1120·0	1118·6	—
	Ni taken, *mg*	Cathode deposit of Ni, *mg*	
7	8·1	8·0	
8	81·0	80·7	
9	162·0	162·4	

* Figures in brackets represent the theoretical weight of $CoSO_4$ assuming the cobalt deposit to be 100% pure.

not impaired even at higher current densities. Less than 10 μg of cobalt were found by the nitroso-R-salt method in the electrolytic bath after deposition. The purity of the cobalt deposit was confirmed by dissolving it and weighing as cobalt sulphate (Table I). The pink colour of the malonate bath suggests that malonate stabilizes cobalt(II) even in ammoniacal solution.

Separation of cobalt from nickel

The difference in behaviour of their complexes with isonitrosomalonic acid can be used to advantage in making an ion-exchange separation of cobalt and nickel. On treatment of a solution of malonic acid with sodium nitrite, nitrous fumes are evolved, followed by the formation of isonitrosomalonic acid.[8] When the reaction is carried out in the presence of cobalt, a deep red solution results which is not affected by the addition of either dilute acid or alkali, unlike isonitrosomalonic acid which is colourless in acid solution. When such a cobalt solution is passed through an anion-exchange column (IRA-400 in the chloride form) the cobalt is quantitatively retained in the

TABLE II.—SEPARATION OF COBALT FROM NICKEL ON AMBERLITE IRA-400*

No.	Co–Ni mixture, *mg*	Ni found, *mg*	Co found, *mg*
1	Ni 100·7		
	Co 115·0	100·8	115·0
2	Ni 5·0	5·1	
	Co 115·0		115·2
3	Ni 100·7	101·0	
	Co 15·0		14·8
4	Ni 1·0	1·01	
	Co 87·1		87·0
5	Ni 100·7	100·0	
	Co 1·0		1·02

*Eluent 100 ml of 2*M* NH_4Cl in dilute ammonia (1 + 4). Linear flow-rate 2 cm/min.

form of an intensely red band. In contrast, when a nickel solution is similarly treated no nickel is taken up by the exchanger. The complex species of cobalt and nickel formed in a malonic acid–nitrite medium thus appear to be dissimilar. The cobalt complex is taken up by the anion-exchanger from solutions of pH between 2 and 10. It is not desirable to have the ion-exchanger initially in the hydroxide form, because of the tendency of nickel to precipitate in the column at high pH. The results obtained for the separation of synthetic mixtures of cobalt and nickel are presented in Table II.

A dilute solution of sodium hydroxide containing sodium chloride fails to elute the cobalt from the column. Presumably, ammonia reacts with the cobalt complex to give a new cobalt species not adsorbed on the anion-exchanger.

Zusammenfassung—Eine Anionenaustauschmethode zur Kobalt-Nickel-Trennung wurde entwickelt auf Grund der Beobachtung, daß aus einer Natriumnitrit enthaltenden Malonsäurelösung Kobalt vorzugsweise vom Austauscher adsorbiert wird, während Nickel durchläuft. Kobalt wird mit 2*M* Ammoniumchlorid in verdünntem Ammoniak eluiert. Aus einer chlorid- und nitrathaltigen Ammonium-malonatlösung wird Kobalt quantitativ elektrolytisch auf einer Platinkathode abgeschieden und gibt einen blanken, gut haftenden Niederschlag. Nickel wird aus einem Bad ähnlicher Zusammensetzung abgeschieden.

Résumé—On a élaboré une méthode par échange d'anions pour la séparation du cobalt du nickel, basée sur l'observation que, à partir d'une solution d'acide malonique contenant du nitrite de sodium, le cobalt est adsorbé préférentiellement par l'échangeur alors que le nickel n'est pas retenu. On élue le cobalt par du chlorure d'ammonium 2*M* en solution ammoniacale diluée. A partir d'une solution de malonate d'ammonium contenant du chlorure et du nitrate, le cobalt se dépose quantitativement par électrolyse sur une cathode de platine en donnant un dépôt brillant et adhérant. Le nickel est déposé à partir d'un bain de composition similaire.

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EMISSION SPECTRA OF NITROUS OXIDE SUPPORTED ACETYLENE FLAMES AT ATMOSPHERIC PRESSURE

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Summary—The emission spectra of a premixed flame of acetylene supported by nitrous oxide have been recorded under different fuel–gas mixture conditions. The emission spectra in these flames of a series of metals, for which it is difficult to obtain a significant population of ground state atoms for atomic absorption spectroscopy in more conventional flames, have also been studied. The red secondary zone which is present in the fuel-rich flames shows emission attributable to long-lived CN and NH species which form a strongly reducing atmosphere to inhibit refractory oxide formation from elements such as molybdenum, titanium and aluminium introduced into the flame. An attempt has also been made to explain some of the reactions which may occur between the flame species above the primary reaction zone.

THE use of flames of acetylene supported by nitrous oxide has been recommended for the determination by atomic absorption spectrophotometry of elements which form refractory oxides in premixed flames of hydrocarbons with air.[1,2] The higher sensitivity which is reported for several elements (*e.g.*, aluminium, titanium, tungsten and molybdenum) when this flame is used instead of luminous air–acetylene flames, probably arises from the production of a larger population of free metal atoms in the ground state when nitrous oxide–acetylene is employed. Little evidence has been presented, however, concerning the cause of the effectiveness of this flame in the production of free metal atoms for atomic absorption spectroscopy. The maximum temperature of a nitrous oxide–acetylene flame burning at atmospheric pressure has been quoted as 2955°.[3] No data are available, however, concerning the region of the flame in which this temperature is found, or the nature of the flame to which this temperature relates (truly stoichiometric, fuel-lean, or fuel-rich). Amos and Willis[2] considered the combustion process in a stoichiometric nitrous oxide–acetylene flame as

$$5N_2O \rightarrow 5N_2 + \tfrac{5}{2}O_2 \ldots \Delta H_{298} = +101{\cdot}5 \text{ kcal}$$

$$C_2H_2 + \tfrac{5}{2}O_2 \rightarrow 2CO_2 + H_2O \ldots \Delta H_{298} = -300{\cdot}1 \text{ kcal}$$

i.e., the nitrous oxide decomposes, and the temperature of the flame is increased by absorption of the energy liberated by the decomposition. The effectiveness for refractory elements of the nitrous oxide–acetylene and oxy-acetylene flames has been ascribed to their high temperatures (2955 and 3060° respectively) compared to that of an air–acetylene flame (2300°). It is difficult to accept an explanation of this type based solely on the improved atomization of the refractory species at these higher temperatures, bearing in mind that to obtain these temperatures more free oxygen is

provided for the acetylene combustion (either directly in oxy-acetylene flames or indirectly by the decomposition of nitrous oxide) than is employed in air–acetylene flames. It might be expected that this increase in the availability of oxygen might favour the formation of refractory species and that this should outweigh the ability of the hotter flame to dissociate the refractory oxides.

It appears that a more important cause of the high population of free atoms could be the existence of sufficient free carbon species in the flame to provide reducing conditions to prolong the lifetime of the larger atomic population produced by the higher temperature. The existence of free carbon itself would aid the production of free atoms by the reaction

$$MO + C \rightleftharpoons M + CO.$$

where MO is the refractory form of metal "M".

A mechanism of this type has already been suggested by Gibson, Grossman and Cooke[4] and also by Amos and Thomas[5] to explain the success of oxy-acetylene flames in the atomic absorption spectrophotometry of elements such as aluminium. Presumably, although they do not specify this, the carbon is provided immediately above the primary reaction zone of the oxy-acetylene flame and manifests itself as the continuous yellow–white luminosity always present in fuel-rich hydrocarbon flames.

The nitrous oxide–acetylene flame, on the other hand, provides good sensitivity for refractory elements without the need for the production of a yellow luminous flame. In slightly fuel-rich flames of nitrous oxide–acetylene a characteristic "red feather" exists between the primary reaction zone and the blue outer diffusion flame. This zone is clearly a secondary reaction zone and has a well-defined "reaction-front" of its own (see Fig. 2b). It is this zone of the flame which is often the most suitable for atomic absorption measurements for many elements.

In an attempt to explain the effectiveness of the nitrous oxide–acetylene flame, in particular the red zone, for atomic absorption work, we have examined spectrographically the emission from various zones of flames of differing compositions, in the presence and absence of elements which form refractory oxides or which are difficult to determine by atomic absorption methods in flames of hydrocarbons mixed with air. Gibson *et al.*[4] have shown that the emission intensity is closely related to the ground-state concentration of the species concerned; hence these investigations are useful in the interpretation of absorption processes in the flame. We have identified the principal molecular and atomic species which exist in each region of the flame, and attempted to account for some of its analytically interesting properties.

EXPERIMENTAL

Apparatus

Nitrous oxide–acetylene burner. This burner has been described previously.[6] It consists of a brass plate, with a slit 0·015 in. wide and 2 in. long, mounted on a brass base and premixing chamber similar to that employed in the air–acetylene burner used on the Unicam SP900A flame spectrophotometer. An air–acetylene mixture was first used in the burner, and the change to nitrous oxide–acetylene effected by gradual replacement of the air by nitrous oxide *via* a T-piece and two rotameters. The sample solutions were introduced *via* a nebulizer and glass expansion chamber and aspiration was *via* the nitrous oxide supply to the flame.

Spectrographic equipment. A Hilger large quartz spectrograph was used for these studies. The burner (B) was mounted on the optical bench so that it was "end-on" *i.e.*, an image of the 0·015–in. side of the burner was presented to the spectrograph (S) and focused either at the slit or the collimating

lens by quartz lenses (L) (Fig. 1). The "end-on" position was used to give more intensity at the spectrograph than when the burner was "broadside" on, but it was realized that there might be self-absorption of radiation from flame species with the burner in this position. Exposures were made on either Kodak or Ilford N.30, B.10 or R.40 plates depending on the wavelength range to be examined and the speed required. The plates were developed in Ilford ID36 developer under standardized conditions, and intensities were measured where necessary with a Hilger photomicrodensitometer. Metals were introduced into the flames as 10^{-1} or $10^{-2}M$ solutions of their nitrates, sulphates or chlorides *via* a Hilger and Watts "Uvispek" nebulizer (A) aspirated by nitrous oxide.

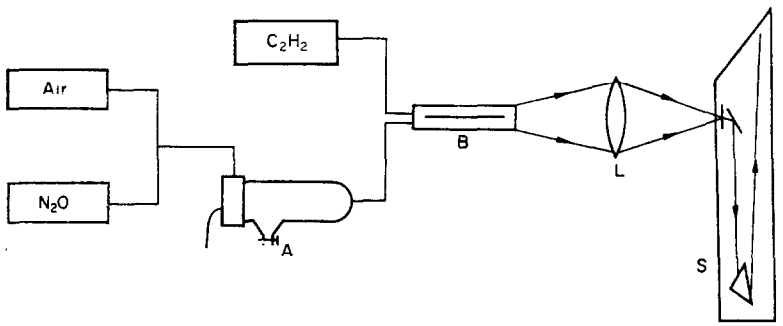

FIG. 1.—Diagrammatic arrangement of apparatus employed.

RESULTS AND DISCUSSION

Flames

Figure 2 shows the appearance of the nitrous oxide–acetylene flames examined.

Lean flames. Lean flames were obtained for nitrous oxide–acetylene with a flow-rate of 3 l/min of nitrous oxide and 1·8 l/min of acetylene. These flames appear as in Fig. 2a and exhibit only two zones, the primary reaction zone which is intensely white–blue in colour, and the outer (or diffusion) zone which is the typical blue colour of all stoichiometric or lean hydrocarbon–air flames. The emission spectra obtained over the range 2800–6700 Å are shown in Fig. 3a. The species identified in the primary reaction zone are OH, NH, CH, CN and C_2. Investigation at wavelengths less than 2800 Å also reveals emission from NO in this zone. The outer cone of these flames

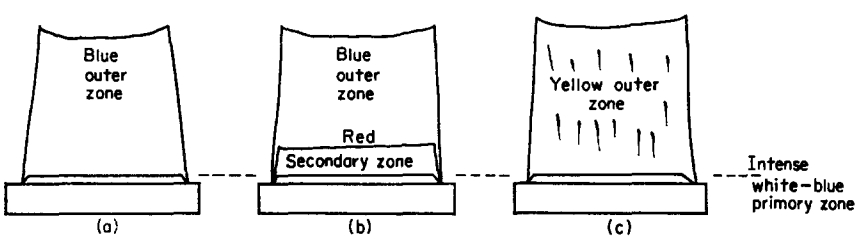

FIG. 2.—Appearance of (a) fuel-lean, (b) slightly fuel-rich, and (c) very fuel-rich nitrous oxide-acetylene flames burning at the rectangular burner (2 in. × 0·015 in. slit).

reveals intense emission only from OH bands at 2811 Å ($^2\Sigma$–$^2\Sigma$ (1, 0)) and 3064 Å ($^2\Sigma$–$^2\Pi$ (0, 0)). Also present in this zone is the continuum emission between 3000 and 5000 Å from the chemiluminescence of the reaction $CO + O \rightarrow CO_2 + h\nu$, which is responsible for the familiar blue colour of the flame. This continuum is overlaid by diffuse bands. Comparison of these lean flame emission spectra with

lean or stoichiometric hydrocarbon–air emission spectra reveals, as expected, that the species present in both zones are the same. The intensity of the band emission from these species, however, is considerably greater in nitrous oxide–acetylene flames, presumably due to the more favourable excitation conditions provided by the higher temperature.

"*Atomic absorption*" *flame.* This flame, which has already been used for the atomic-absorption spectrophotometry of several elements, was obtained with a flow-rate of 3 l/min of nitrous oxide and 2 l/min of acetylene. The flame, which is slightly fuel-rich, consists of three distinct zones as shown in Fig. 2b. These are (1) the intensely white–blue primary reaction zone, (2) the "red-feather" zone, and (3) the outer zone. A typical emission spectrum from this flame over the range 2800–6700 Å is shown in Fig. 3b. The species present in the primary reaction zone are again, as for the lean flame, the same as those present in most premixed flames of hydrocarbons burning with air. The outer diffusion zone also again exhibits emission from OH, although this is not as intense as in fuel-lean flames. The CO continuum is also weakened, as would be expected, as less oxygen is presumably available for its combustion with emission of chemiluminescence. The "red-feather" zone, which exists between the primary and outer zones, has a well-defined front of its own and appears as a separate reaction zone. With the burner used the height of this red zone could be as much as 2 cm, and was proportional to the amount of acetylene supplied to the flame. As can be seen in Fig. 3b, the species which predominate in this zone are CN and NH. The CN violet band system is clearly visible. This system is degraded towards the violet and has very well marked sequences. The (0, 0) sequence at 3883 Å is the strongest. The (0, 1) sequence of CN at 4216 Å, which is often obscured by CH unless it is very strong, is clearly visible, free from masking from the nearby CH (0, 0) system at 4315 Å which only appears at the bottom of the red zone. The intense (1, 0) sequence of CN at 3590 Å is present in this red zone and is clear from major overlapping features. This sequence often shows in hot flames containing nitrogen. Some sequences of the CN red system, which are not usually observed in flames with air, are emitted strongly in the red zone. Heads at 5730 Å (6, 1), 5858 Å (7, 2), 6191 Å (4, 0), 6332 Å (5, 1) and 6468 Å (6, 2), similar to those obtained in burning cyanogen,[7] are clearly visible. Emission assignable to CH is also present in this zone, but is restricted to the lower part of the red zone, immediately above the primary zone. The 4315 Å CH system is the strongest and is due to a $^2\Delta$–$^2\Pi$ transition. It is degraded towards shorter wavelengths, but only weakly. The 3900 Å system ($^2\Sigma$–$^2\Pi$) of CH is also visible, fairly strongly degraded towards the red so that its rotational structure appears more open than that of the 4315 Å system. The weakest sequence of CH in most flames is that at 3143 Å. This system is not easily observed in the red zone (but is clearly seen in the primary cone). This band is usually partly obscured by the strong rotational structure of the OH 3064 Å band, but can just be observed at 3143 Å at the expected intensity maximum from the Q branch. C_2 emission, like CH, is also present in the lower part of the red zone immediately above the reaction zone. The C_2 bands are degraded towards the violet and show well-marked sequences, the (1, 0), (0, 0) and (0, 1) sequences having heads at 4737, 5165 and 5635 Å. Only the strongest (0, 0) sequence of NH at 3360 Å ($^3\Pi$–$^3\Sigma$) is observed, but the intense emission from this is present throughout the whole of the red zone. Investigation of the emission from the base of the red zone

3

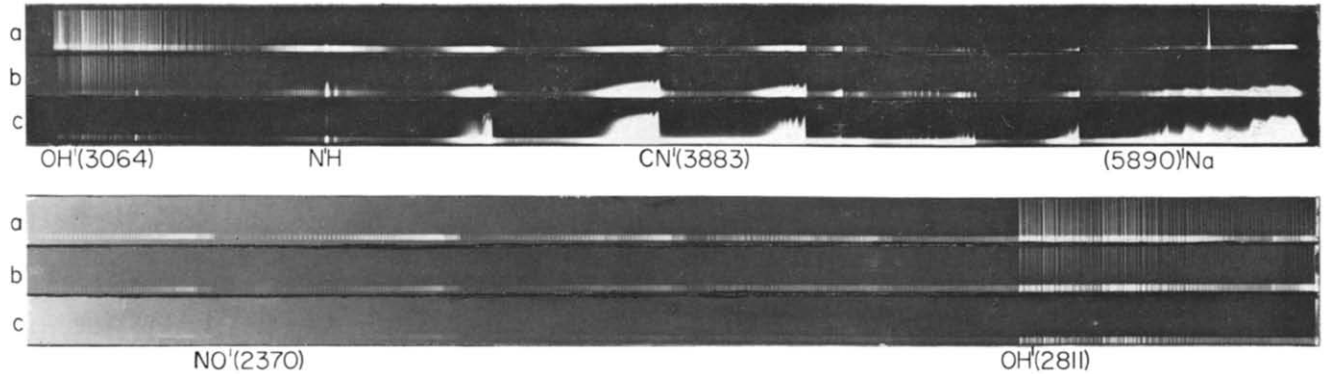

FIG. 3.—Emission spectra of N_2O–acetylene flames. (a) fuel-lean, (b) slightly fuel-rich, and (c) very fuel-rich.

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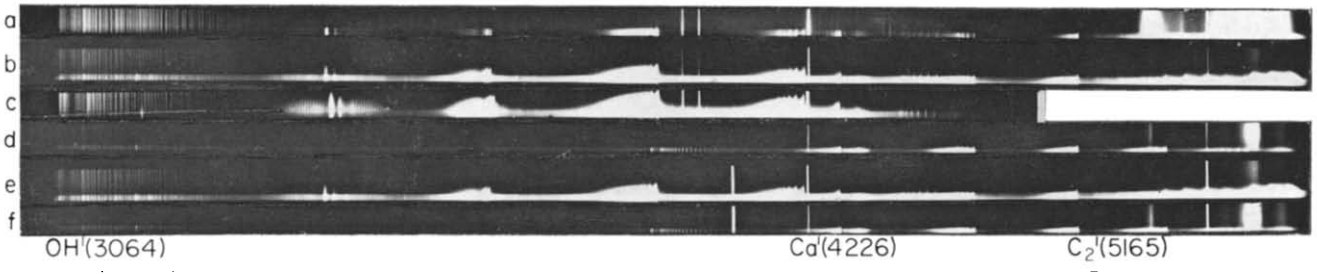
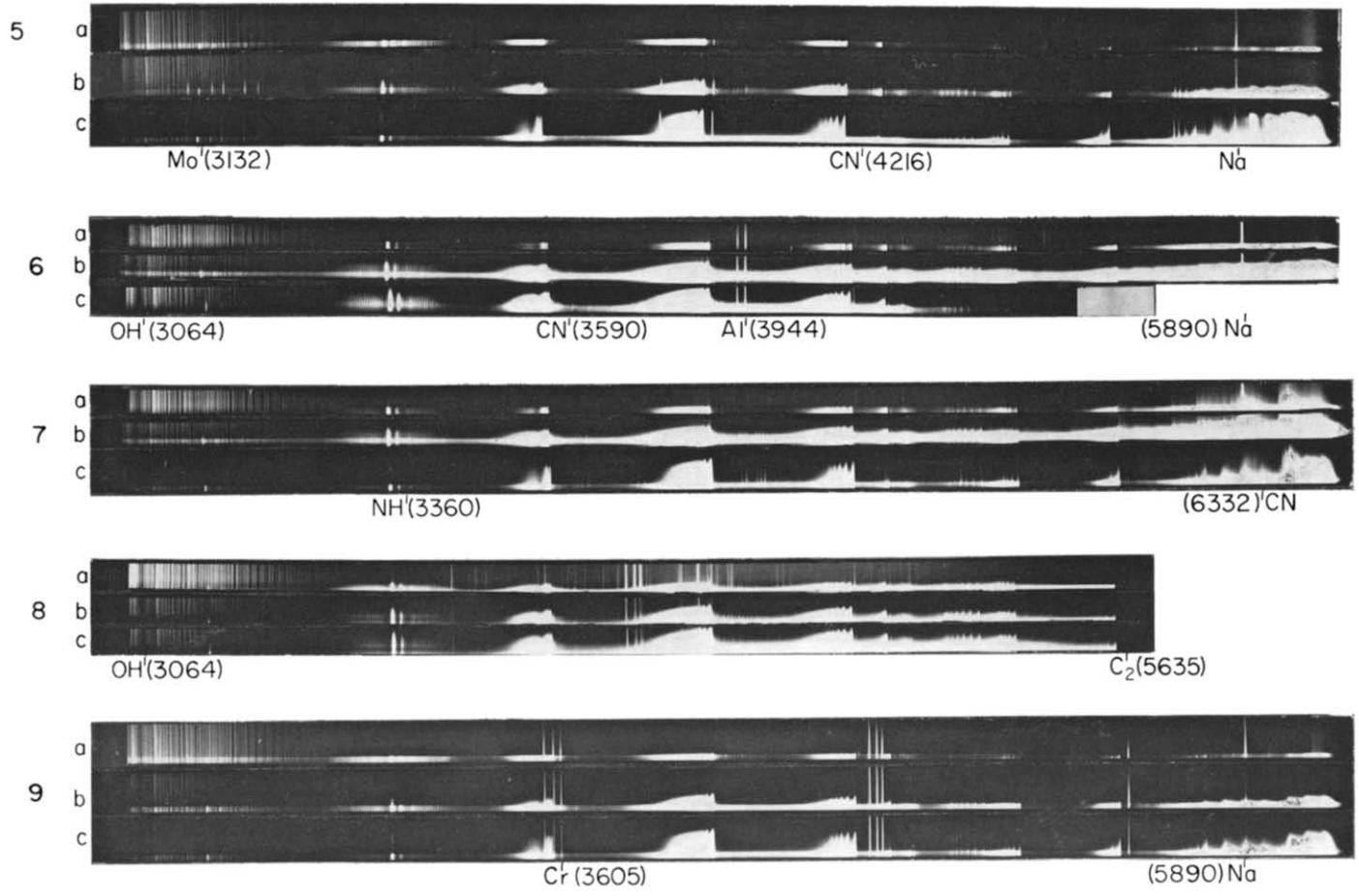
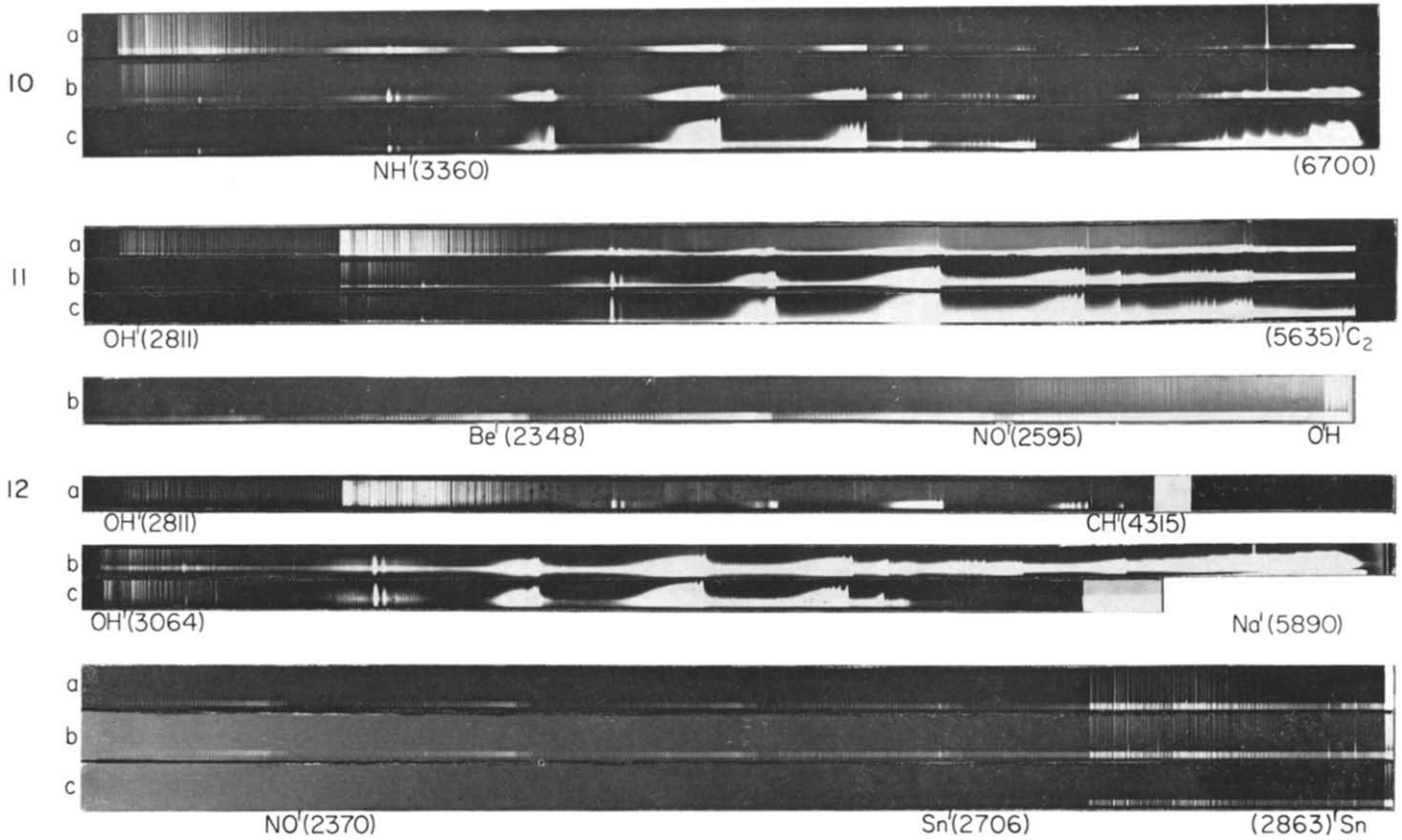


FIG. 4.—Emission spectra of calcium in flames. (a) fuel-lean N_2O–acetylene; (b) slightly fuel-rich N_2O–acetylene; (c) very fuel-rich N_2O–acetylene; (d) air–acetylene; (e) slightly fuel-rich N_2O–acetylene + KCl; (f) slightly fuel-rich air–acetylene + KCl.


5
a
b
c
Mo'(3132)
CN'(4216)
Na'
6
a
b
c
OH'(3064)
CN'(3590)
Al'(3944)
(5890) Na'
7
a
b
c
NH'(3360)
(6332)'CN
8
a
b
c
OH'(3064)
C'2(5635)
9
a
b
c
Cr (3605)
(5890) Na'



(a) fuel-lean, (b) slightly fuel-rich, and (c) very fuel-rich.

FIG. 5.—Emission spectra of molybdenum in nitrous oxide–acetylene flames.
FIG. 6.—Emission spectra of aluminium in nitrous oxide–acetylene flames.
FIG. 7.—Emission spectra of titanium in nitrous oxide–acetylene flames.
FIG. 8.—Emission spectra of iron in nitrous oxide–acetylene flames.
FIG. 9.—Emission spectra of chromium in nitrous oxide–acetylene flames.
FIG. 10.—Emission spectra of vanadium in nitrous oxide–acetylene flames.
FIG. 11.—Emission spectra of beryllium in nitrous oxide–acetylene flames.
FIG. 12.—Emission spectra of tin in nitrous oxide–acetylene flames.

at wavelengths less than 2800 Å reveals the presence of the bands of the γ system of NO with heads at 2370 Å (0, 1), 2478 Å (0, 2) and 2595 Å (0, 3). The NO head at 2478 Å prevents the detection of the atomic carbon line reported to appear at 2478 Å in some very hot flames of carbon-rich fuels. The emission from OH at 3064 and 2811 Å in this zone is weaker than that in the primary and outer zones. It thus appears that the species responsible for the visible "red feather" is CN, which, along with NH, persists through the whole zone and is present in great abundance. At the base of the red zone, immediately above the primary reaction zone, C_2, CH and NO are also present and the OH emission is weak.

Fuel-rich flame. This flame was obtained with a flow-rate of 3 l/min of nitrous oxide and 2·3 l/min of acetylene. The flame appears as in Fig. 2c, and consists of two visible zones, the primary reaction zone and the intensely luminous outer cone. The primary combustion zone is not easily observed visually, and, although identifiable in the emission spectrum, no red emission zone can be seen. The yellow luminosity from carbon particles tends to mask the whole flame. The emission spectrum of this flame is shown in Fig. 3c. The visible region, between *ca.* 3600 and 6700 Å is overlaid by intense continuum emission from the incandescent carbon particles. Little difference is observed in the spectra of the primary and secondary zones from those of the slightly fuel-rich flames, with the exception that the γ NO system in the primary cone is weakened in this very fuel-rich flame. It is possible to distinguish the principal bands of CN and NH which presist very high in the flame. Weak C_2 emission is also present throughout the greater part of the flame length. Emission from OH and CH is very weak throughout the whole flame. The red emission of the CN bands at 5730 Å and above is obscured by the luminous carbon continuum. From these observations on the emission from the reaction zones of the different flames, it is possible to suggest an explanation of the analytically useful properties of the red zone in slightly fuel-rich flames. The CN and NH bands which persist through this zone, and the C_2 and CH bands in the lower part of the zone, occur when there is not sufficient oxidant in the mixture to convert all the carbon into carbon monoxide. Under these reducing conditions the CN and NH molecules formed in the reaction zone and above have an unusually long life-time. The OH emission in the lower part of the red zone is weakened, and the position of this weakening coincides with the disappearance of C_2 and CH species, probably by the reactions

(*a*) $$C_2 + OH \rightarrow CO + CH$$

(*b*) $$CH + OH \rightarrow CO + H_2.$$

There is strong evidence to suggest that much of the CH is produced from C_2 (as in *a* above) in hydrocarbon flames,[8] although the reaction path is not known with certainty. The red zone exhibits a clearly defined "reaction front" similar to those observed by Parker and Wolfhard[3] in other flames supported by oxides of nitrogen. The formation of more than one reaction zone is frequently linked with the fact that different reactions begin at different temperature levels in the combustion wave. Our evidence suggests that the nitrous oxide is not all decomposed to N_2 and O_2 in the primary reaction zone. It seems that appreciable quantities of NO are formed, either directly at the primary reaction front from N_2O or more probably as a product from the initial reaction of an acetylene molecule with N_2O. This latter

mechanism is suggested by the strength of the band systems of species containing nitrogen (CN, NH) in the flame which cannot be satisfactorily explained if decomposition of N_2O proceeds directly to N_2 and O_2.[8] The γ NO system is quite strong in and slightly above the primary zone. Little, if any, atomic oxygen is present in the red zone. The test for atomic oxygen in flames is to add small amounts of nitric oxide to the flame gases before combustion, and if atomic oxygen is present the continuum emission from the reaction $NO + O \rightarrow NO_2 + h\nu$ is always seen.[9] This continuum extends from *ca.* 4000 Å to the near infrared but is strongest in the yellow and green regions. Despite the significant emission from NO low in the zone, no trace of a continuum from atomic oxygen can be detected.

The red zone is not in itself a "diffusion" flame, and does not depend on the diffusion of oxygen in from the atmosphere or through the outer zone as does the burning of CO in the outer blue diffusion zone itself. This may be demonstrated by sheathing the whole flame in an atmosphere of argon, when no change in the appearance of the red zone is observed. The reaction front of the red zone thus appears similar to that of a premixed flame in nature, *i.e.*, the reactants are both present "behind" the reaction front.

The high concentration of CN and NH in the fuel-rich flames must result from the way in which the nitrous oxide reacts initially with an acetylene molecule. The long life-time of the reducing CN and NH species may then be attributed to the lack of sufficient oxidant in the form of OH or NO to consume these species rapidly. Thus reactions of the following type may account for the slow consumption of CN and NH.

$$CN + OH \rightarrow CO + N + H \quad \text{or} \quad CO + NH \tag{1}$$

$$NH + OH \rightarrow H_2 + NO \quad \text{or} \quad H_2O + N \tag{2}$$

$$CN + NO \rightarrow CO + N_2 \tag{3}$$

$$NH + NO \rightarrow OH + N_2 \tag{4}$$

The reactions (1) and (2) could explain the weakening of OH intensity in the red zone, and also account for the similar life-time of CN and NH due to reaction with the same species. Reactions (3) and (4) could also account for the slow consumption of CN and NH, and the disappearance of NO in the red zone and from the primary zone in very fuel-rich flames. These last reactions could also lead to a similar life-time of CN and NH owing to reaction with the same NO species whose production is dependent upon the decomposition of nitrous oxide in the primary zone.

It may be, however, that the combustion mechanism is better explained in the way suggested by Parker and Wolfhard[3] to account for the double reaction zones shown by hydrocarbon flames supported by nitrous oxide and nitrogen dioxide. Flames of hydrogen, for example, burning with a mixture of nitrous and nitric oxides show two reaction zones, and the second upper reaction zone is thought to coincide with the burning of hydrogen with nitric oxide which requires a higher temperature than the hydrogen–nitrous oxide reaction. The situation might be complicated by this type of effect in the nitrous oxide–acetylene flame, in which the nitric oxide produced in the primary zone does not react with degraded fuel molecules until well above this zone.

It seems certain that the effectiveness of the fuel-rich flame for atomic-absorption

spectrophotometry of refractory elements is not solely due either (*a*) to the high temperature available for refractory oxide dissociation, or (*b*) to the existence of "free" carbon for the reaction $MO + C \rightarrow M + CO$ to occur as suggested for luminous oxygen–acetylene flames by Gibson[4] and Amos and Thomas.[5] It will be seen from our results for elements such as molybdenum, that emission from the principal resonance lines occurs only in relatively fuel-rich nitrous oxide–acetylene flames and not in fuel-lean flames. For the nitrous oxide–acetylene flame, however, as for many hydrocarbon–air flames, the temperature and burning velocity are actually *lower* in fuel-rich flames than in fuel-lean flames. The red zone is virtually free from the incandescent carbon continuum. The reaction $MO + C_2 \rightarrow M + CO + C$ is possible at the base of the red zone, but C_2 emission is probably chemiluminescent and its actual concentration is low. Amos and Willis[2] made a comparison of nitrous oxide–acetylene and oxygen–nitrogen–acetylene flames for the atomic absorption spectrophotometry of many elements. They obtained similar sensitivities in the two flames for many refractory elements, and seem to ascribe this similarity to the similar high temperatures of the two flames. It appears, however, that the actual mechanisms by which the atmosphere of ground state atoms of the elements is maintained in these flames is different. It seems probable that in slightly fuel-rich luminous nitrogen–oxygen–acetylene flames the production of metal atoms from the oxide is assisted *via* the $MO + C \rightarrow CO + M$ reaction, and that in the red zone of the nitrous oxide–acetylene flame at a similar temperature the metal atom is protected by the extremely reducing atmosphere of CN and NH. When metal oxide is formed in the primary zone or above, it may also be attacked by NH or CN at this high temperature to provide free atoms by reactions of the type:

$$MO + NH \rightarrow M + NO + H \quad \text{or} \quad M + OH + N$$

$$MO + CN \rightarrow M + CO + N.$$

Emission spectra of metals in the flame

The emission spectra of the fuel-lean, slightly fuel-rich and very fuel-rich flames were recorded in the presence of a series of metals introduced into the flame as aqueous solutions of their simple salts. The metals chosen for examination were some of those elements which are difficult or impossible to determine by absorption spectrophotometry in flames burning with air owing to total or partial lack of atomization because of the formation of refractory oxides or other species. The emission spectra yield information concerning the existence and position in the flame of free excited atoms as well as molecules such as CaOH. The intensity of the emission is closely related to the ground-state concentration of the species concerned at any given temperature, and thus information on position and intensity of thermal emission is useful in the study of absorption processes.

Calcium. The emission spectra of the nitrous oxide–acetylene flame burning under the three fuel conditions in the presence of calcium are shown in Fig. 4. The calcium emission in a fuel-lean flame (Fig. 4a) resembles that in a hydrocarbon–air flame. Amos and Willis[2] have reported greater sensitivity for calcium in nitrous oxide–acetylene than in air–acetylene flames, and attributed this to more complete atomization. The presence, even in this flame, of much incompletely atomized calcium can be seen from the intense band emission at 5498 and 6097 Å attributable

to CaOH.[11] The 4226 Å line which is most commonly used for the determination of calcium by atomic absorption, is very intense throughout the whole length of the flame. The strong lines at 3933·7 and 3968·5 Å correspond to emission from singly ionized calcium atoms, Ca^+. The strength of these lines bears out the observation of Amos and Willis[2] concerning the high degree of ionization in this flame compared to air–acetylene flames. They estimate the ionization for calcium to be 43% in nitrous oxide–acetylene and 3% in air–acetylene. Figure 4d shows the emission spectrum of calcium in the corresponding air–acetylene flame, in which the ion lines are barely detectable. Figures 4e and 4f show the effect on calcium emission in slightly fuel-rich nitrous oxide–acetylene and air–acetylene flames of the addition of excess of potassium chloride. Potassium is more easily ionized than calcium, and the high concentration of electrons formed by the reaction $K \rightarrow K^+ + e$, tends to reverse the ionization $Ca \rightarrow Ca^+ + e$. The calcium lines at 3933·7 and 3968·5 Å are not visible in the nitrous oxide–acetylene flame in the presence of potassium, indicating virtually complete suppression of ionization. Ionization of calcium in its determination by atomic-absorption spectrophotometry leads to some curvature away from the concentration axis, and a linear curve may thus be obtained by adding potassium.

The calcium emission spectra from slightly fuel-rich and fuel-rich flames (Figs. 4b and 4c) are very similar. The principal difference in these spectra compared to that from a fuel-lean flame is that the CaOH band at 5498 Å is somewhat less broad, suggesting that the highly reducing nature of the flame results in more complete atomization. Some broadening of the CaOH bands on the spectrographic plate is also evident higher in the flame, possibly due to the production of more CaOH in this region by a three-body recombination reaction.

Molybdenum. The emission spectra of flames containing molybdenum are shown in Fig. 5a, b and c. In fuel-lean flames (Fig. 5a) no lines of molybdenum are observed. A diffuse continuum exists around 5600 and 6500 Å in the outer cone which is attributable to the species MoO.[12] In slightly fuel-rich flames (Fig. 5b) the molybdenum lines at 3132·6, 3158·2, 3170·3 and 3194·0 are strong and persist throughout the red zone of the flame, as do the strong lines at 3798·3, 3864·1 and 3903·0 Å. Several other lines are also weakly visible in the red zone, but no line emission occurs above this cone. In a very fuel-rich flame (Fig. 5c) the same lines are visible but persist throughout a greater length of the flame.

Aluminium. Figures 6a, b and c show the emission spectra of aluminium introduced into the nitrous oxide–acetylene flames. In the fuel-lean flame (Fig. 6a) only two strong lines are obtained, at 3944·0 and 3961·5 Å, and these are present over most of the length of the flame. The aluminium doublet at 3092·7 Å, which has been used for the determination of aluminium by atomic absorption in a nitrogen–oxygen–acetylene flame,[5] cannot be detected. The outer zone of the flame exhibits a series of moderately strong bands with heads at 4470·5, 4648·2, 4842·1 and 5079·3 Å and a weak one at 5336·9 Å. These bands have been attributed to the vibrational structure within the ground state $B^2\Sigma$–$^2\Sigma$ (ground state) electronic transition for AlO.[13] In slightly fuel-rich flames (Fig. 6b) these bands of AlO are weakened considerably and only the strongest at 4648·2, 4842·1 and 5079·3 Å are visible. The 3944·0 and 3961·5 Å lines are clearly visible, and appear more intense than in the fuel-lean flame. Although partly obscured by the OH bands at 3064 Å, the aluminium resonance

lines at 3082·2 and 3092·7 Å can be distinguished in the red zone. The fuel-rich flame spectrum (Fig. 6c) is similar, and the lines at 3082·2 and 3092·7 Å appear only slightly more intense than in the red-zone flame. The AlO bands, however, are barely visible in the fuel-rich flame.

Titanium. The titanium emission spectra in the different flames are shown in Figs. 7a, b and c. The behaviour of this element in the nitrous oxide–acetylene flame is similar to that of aluminium. Only bands due to TiO are found in fuel-lean flames. Some of the bands of the γ red system of TiO are present above 6215 Å, but most of the sequences of this strong system lie outside the upper limit of the investigation above 6800 Å. Sequences of the α blue-green system of TiO, where the electronic transition is $^3\Pi$–$^3\Pi$, ground state,[14] are present with a complex series of heads between 4462·1 and 6214·9 Å. Superimposed on these bands are those of the TiO orange system (β) with heads between 5597·8 and 5694·4 Å. No resonance lines of titanium are observed in this flame. In slightly fuel-rich flames (Fig. 7b) the TiO band systems are weakened in the outer zone, but are obscured to some extent by the C_2 and CN emission. Many resonance lines of titanium appear in the red zone, but not above, and the strongest appear at 3635·5, 3642·7 and 3653·5 Å. The appearance of this spectrum suggests that the slightly fuel-rich nitrous oxide–acetylene flame should enable titanium to be determined readily if the light path of the radiation from the source is restricted to pass within the red zone. The fuel-rich flame spectrum (Fig. 7c) is similar, with the exception that the Ti lines persist higher in the flame, and the TiO band spectrum is weakened further.

Iron. The iron flame emission spectra are shown in Figs. 8a, b and c. Very little difference is seen between fuel-lean, slightly fuel-rich and very fuel-rich flames. More of the principal resonance lines of iron are present over most of the flame length in nitrous oxide–acetylene than in the corresponding air–acetylene flames, presumably because of the higher temperature. Very little difference in the line intensities is observed in the flame under the different conditions. It is possible, therefore, that a fuel-lean flame might yield better precision (perhaps at some loss of sensitivity) for the determination of iron by atomic absorption spectroscopy in nitrous oxide–acetylene, owing to lack of background radiation from CN, CH and C_2. The continuum CO emission in the outer cone of the fuel-lean flame should not provide a source of noise as great as the other flame species containing carbon.

Chromium. The chromium emission spectra in the nitrous oxide–acetylene flame under different flame conditions are shown in Figs. 9a, b and c. As with iron, the spectra are similar. Two intense groups of three lines appear at 3578·7, 3593·5, 3605·3 and 4254·3, 4274·8, 4289·7 Å. The lines which have been used for the atomic absorption spectrophotometry of chromium in air–acetylene flames (3578·7 and 3593·5 Å) lie on the 3590 Å CN sequence in the fuel-rich nitrous oxide–acetylene flame. Our experience shows that greater sensitivity for chromium is obtained in the red zone than above it, or in fuel-lean flames. The noise levels at the 3578·7 and 3593·5 Å lines, however, even with a modulated hollow-cathode source and tuned amplifier, are too great to allow good precision. The 3605·3 Å line should provide good sensitivity with less background noise, and the 4254·3 Å line should give even less noise but probably less sensitivity.

Vanadium. The vanadium emission spectra are shown in Fig. 10a, b and c. In the fuel-lean flame no strong lines are observed above the primary reaction zone,

although the vanadium lines at 3066·4, 3183·4, 3184·0 and 3185·4 Å may show weak emission but are not distinguishable against the strong OH emission in this region. In slightly fuel-rich flames, the persistent lines at 3183·4, 3184·0 and 3185·4 Å are observed at the base of the red cone (and higher in very fuel-rich flames) against the weakened OH emission. The 3703 Å line, and the group of three lines at 4379·2, 4384·7 and 4390·0 Å, are clearly visible and persist in the reducing atmosphere. Because of the intense CN emission at the wavelengths concerned it is not possible to determine whether the vanadium lines at 3840·0 and 3855·8 Å examined by Amos and Willis[2] are present. No clearly assignable bands of the VO species can be detected. It seems that the determination of vanadium by atomic absorption spectrophotometry would be best conducted at 3184·0 Å in fuel-rich flames immediately above the reaction zone where OH noise is minimal.

Beryllium. Figures 11a, b and c show the emission spectra of beryllium introduced into the different flames. The fuel-lean flame (Fig. 11a) shows a strong band with a head at 4708 Å and a weak sequence with a head at 4427 Å attributable to the (0, 0) and (1, 0) vibrational bands within the $C^1\Sigma \rightarrow X^1\Sigma$ electronic transition of the blue-green system of BeO.[15] No beryllium resonance lines are observed. In slightly fuel-rich flames, however, the beryllium resonance line at 2348·6 Å is visible in the red zone, but this atomic emission is short-lived and does not persist to the top of the red cone. The BeO band at 4708 Å is not detectably weaker in this flame than in the fuel-lean flame. In the very fuel-rich flame (Fig. 11c) the Be line at 2348·6 Å is not easily observed, even against the weakened NO emission of the primary zone. The determination of beryllium in nitrous oxide–acetylene by atomic absorption would therefore appear most favourable at the base of the red zone in slightly fuel-rich flames.

Tin. The emission spectra of tin in the different flames are shown in Figs. 12a, b and c. In the fuel-rich flame the most prominent features are lines attributable to iron and chromium impurities. The persistent tin lines are not shown in the ultraviolet below 3300 Å above the primary zone. In the slightly fuel-rich flame (Fig. 12b), however, the atomic lines at 2354·8, 2429·5, 2546·6 and 2706·5 Å and the lines at 2840·0, 2863·3, 3175·1 and 3262·3 Å are visible in the red zone. The lines at 3009·1 and 3034·1 Å are quite strong and persist above the red zone. Any lines above 3262·3 Å are obscured by the flame emission bands. No definite band emission assignable to SnO, SnH or SnCl is observed in these flames. The fuel-rich spectrum (Fig. 12c) is similar, but the emission from the lines mentioned is stronger and longer-lived.

CONCLUSIONS

Our results suggest that the reactions which occur in the nitrous oxide–acetylene flame to provide and maintain an atomic population for refractory elements are somewhat more complex than can be explained by the reducing action of incandescent carbon particles which has been postulated to explain the action of the oxy-acetylene flame. In summary, it appears that nitrous oxide decomposes to provide oxygen at the primary reaction zone to raise the temperature and burning velocity of the flame. Some of the nitrous oxide decomposes to form nitric oxide and this, or the nitrous oxide itself, appears to react directly with fuel molecules in the primary zone to produce more CN and NH than are produced in a conventional hydrocarbon–air

flame. The life-time of these species is prolonged in regions well above the reaction zone, in the red zone, and in very fuel-rich flames, because of the lack of sufficient oxidant and owing to their slow rate of consumption by OH and possibly NO. A reducing atmosphere is thus provided to protect the metal atoms produced in the primary reaction zone by the high temperature. It is also possible that metal-oxide species produced may be reduced above the primary zone by the CN and NH species. As the flame is made very fuel-rich the reducing conditions due to CN and NH persist higher in the flame and their protective reducing action is supplemented by that of free incandescent carbon particles. It seems probable, from the results obtained on the introduction of metal ions into the flame, that very fuel-rich nitrous oxide–acetylene flames can provide good sensitivity in the atomic absorption spectrophotometry of refractory elements without the need for a limited flame area technique where radiation from the source is passed through the red zone of a slightly fuel-rich flame.

Acknowledgement—We are grateful to the Ministry of Aviation for financially supporting this research project.

Résumé—Les spectres d'emission d'une flamme préalablement mélangée d'acétylène porté par du protoxyde d'azote ont été enregistrés dans différentes conditions de mélange avec du gaz combustible. On a aussi étudié les spectres d'émission dans ces flammes d'une série de métaux pour lesquels, dans des flammes plus usuelles, il est difficile d'obtenir une population importante d'atomes à l'état fondamental pour la spectroscopie d'absorption atomique. La zone rouge secondaire qui est présente dans les flammes riches en combustible montre une émission attribuable aux espèces CN et NH de longue vie, qui forment une atmosphère fortement réductrice inhibant la formation d'oxyde réfractaire à partir d'éléments tels que le molybdène, le titane et l'aluminium introduits dans la flamme. On a aussi tenté d'expliquer quelques-unes des réactions qui peuvent se produire entre les espèces de la flamme au-dessus de la zone de réaction primaire.

Zusammenfassung—Die Emissionsspektren einer vorgemischten Flamme aus Acetylen und Distickstoffoxid wurden bei verschiedene Mischungsverhältnissen registriert. Auch die Emissionsspektren einiger Metalle wurden in solchen Flammen untersucht, bei denen es in gebräuchlicheren Flammen schwierig ist, eine wesentliche Anzahl von Atomen im Grundzustand für die Atomabsorptions-Spektroskopie zu erhalten. Die rote Sekundärzone in acetylenreichen Flammen zeigt Emission langlebiger CN- und NH-Spezies, die eine stark reduzierende Atmosphäre bilden und damit die Bildung feuerfester Oxide zum Beispiel aus Molybdän, Titan und Aluminium verhindern. Es wurde auch versucht, einige der Reaktionen zu erklären, die sich zwischen den Flammen-spezies oberhalb der primären Reaktionszone abspielen können.

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CONCENTRATION AND SEPARATION OF INDIUM, GALLIUM, THALLIUM, ANTIMONY AND BISMUTH BY EXTRACTION WITH ALKYLPHOSPHORIC ACIDS

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Summary—The use of alkylphosphoric acids for solvent extraction separations is described, and the use of antisynergic agents for stripping is discussed.

ALKYLPHOSPHORIC acids (APA) have found a practical application in the production technology of uranium, thorium, vanadium, scandium and indium, where they are used for the extraction, separation, and concentration of actinides and lanthanides. This class of extracting agents appears to be of much promise in the production of high-purity metals and their compounds, as well as for purely analytical use, because of the following factors: they give high distribution coefficients in extractions from solutions of different oxy-acids over a wide range of concentrations; the distribution coefficients do not decrease with a decrease in the concentration of the metal being extracted; it is possible to strip the extracts selectively with salts, acids, and mixtures of acids with antisynergic agents; they have low solubility in mineral acids.

We have studied the extraction mechanisms for gallium, indium, thallium(III), antimony(III) and (V), bismuth, and tin(II) and (IV), and the role of diluents and antisynergic agents. We have also examined the analytical possibilities of APA, using chiefly 1 *N* solutions of mono-2-ethylhexylphosphoric acid (MEHPA) and di-2-ethylhexylphosphoric acid (DEHPA) in heptane, and also a 1*N* mixture of pyro-2-ethylhexylphosphoric acids (PEHPA) in heptane. Certain problems can be solved by changing the extractant used, since in many cases the three acids behave differently.

Extraction from solutions of oxy-acids

As can be seen from Fig. 1, the extraction of gallium, indium, thallium(III), antimony(III), bismuth and tin(IV) by APA from sulphuric acid solutions is practically quantitative over a wide range of acid concentration, and (which is also of importance) over a wide range of metal concentration. This behaviour can be made use of both for the extraction separation of micro-quantities of the metal to be determined, and for removal of the matrix element. The equilibrium in the extraction of indium, gallium, thallium(III), antimony(III), bismuth and tin(II) is established in 20–30 sec, and in 60–70 min for the extraction of antimony(V) and tin(IV). Figure 2 shows that the nature of the APA is of decisive importance for the extraction of gallium, thallium and bismuth.

All the metals mentioned above can be separated by extraction from almost any quantity of the following elements, which are characterized by their low extractability into APA from acid media: alkali and alkaline earth metals, copper, zinc, iron(II),

cobalt, nickel, manganese(II) or (VII), mercury, arsenic(III) or (V), selenium, tellurium, germanium, chromium(III) or (VI), silver, gold, platinum metals,[1–3] and also lead if the latter is extracted from perchloric or nitric acid solution. This holds, with minor variations, for nitric and perchloric acid media as well as for sulphuric acid.

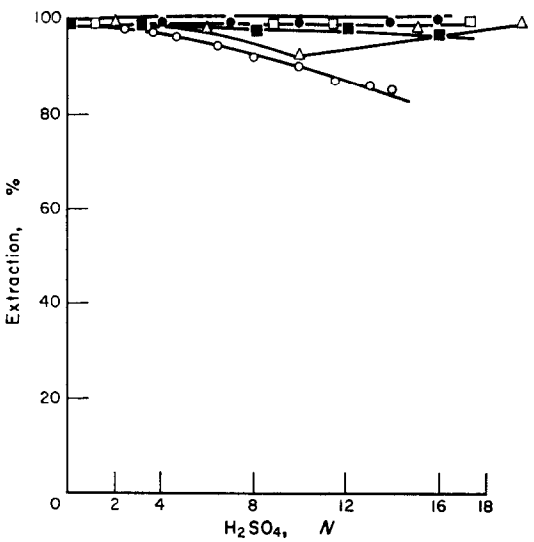

FIG. 1.—Effect of sulphuric acid concentration on extraction with PEHPA.
○—Sb(III); △—Ga; ●—Tl(III); □—In; ■—Bi.

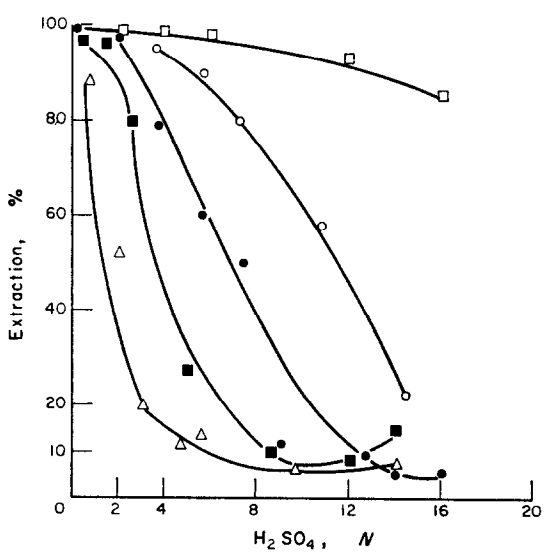

FIG. 2.—Effect of sulphuric acid concentration on extraction with DEHPA.
○—Sb(III); □—In; ●—Tl(III); △—Ga; ■—Bi.

It is difficult, however, to strip some of the metals extracted, and hydrofluoric acid is usually required as stripping agent. Such metals reduce the capacity of the extractant and are considered as "poisons" in technological processes. In analysis,

on the other hand, this creates additional possibilities for their separation. In certain cases, gallium, indium, thallium, antimony(III) and bismuth can be separated at the stripping stage from titanium, zirconium, hafnium, selenium, thorium, tin(IV) and iron(III). Oxalate does not interfere with the extraction of indium and tin(II) or (IV),[4] but prevents the extraction of antimony and bismuth;[5] it can therefore be used as stripping agent in the separation of these metals.

Extraction from hydrohalic acid media

With halide ions, the metals gallium, indium, thallium(III), antimony(III), bismuth and tin form anionic complexes which are weakly extractable into APA, and in several instances hydrohalic acids can be used as efficient stripping agents, permitting manifold concentration of these metals. The degree of concentration that can be achieved is limited by the minimum volume of stripping agent permissible analytically. Antimony(III), indium, gallium and tin(II) or (IV) are extracted quantitatively from dilute hydrochloric acid; even hydroxide and basic salt precipitates do not affect the extraction. Intensive shaking leads to a rapid shift of the equilibrium and the disappearance of the precipitate. With increase in the concentration of hydrochloric or hydrobromic acid, the extractability falls sharply. The distribution coefficients (D) sometimes decrease with change in the acid in the order HCl—HBr—HI—HF, and sometimes in the reverse order. Thus for extraction from isomolar solutions of the hydrohalic acids, the order of the D values is:

$$\text{In—HI} \gg \text{HF} > \text{HBr} > \text{HCl}$$
$$\text{Sb(III)—HCl} > \text{HBr} > \text{HI} > \text{HF}$$
$$\text{Sn(II)—HF} \gg \text{HBr} > \text{HCl}$$
$$\text{Sn(IV)—NBr} > \text{HCl} \gg \text{HF}$$
$$\text{Bi—HCl} > \text{HBr} > \text{HI}.$$

The behaviour of bismuth and thallium(III) in extractions from hydrohalic acid or halide solutions is peculiar; they are not extracted into APA even from solutions containing comparatively minor concentrations of chloride, bromide or iodide, and appear to form halide complexes of the type $MeHal_x^{(m-x)+}$ where m is the charge on the metal ion. Antimony(V) also shows unusual behaviour, being easily extracted with MEHPA or DEHPA from high or low concentrations of hydrohalic acid, but not from medium concentrations (Fig. 3). If only the right-hand branch of the extraction curve was observed, it could be interpreted as indicating the presence of strongly hydrolysed ionic or molecular species in the aqueous phase, but the existence of the left-hand branch, showing that extraction occurs even if hydroxide or basic salt precipitates are present, can only be explained by a change in the mechanism of extraction, from chelate formation to production of molecular species, as happens with tributylphosphate. The behaviour of gallium and thallium also seems anomalous but for gallium this is only so if the extractant is DEHPA (Fig. 4). The behaviour of thallium(III) is the same for all three extractants.

We have shown that in extraction of gallium and antimony(V) from weakly acidic solutions an exchange reaction is involved and that the amount of halide found in the organic phase is insignificant, whereas from strongly acidic media the organic phase extracts molecular species such as $HGaCl_4 \cdot n$DEHPA and $HSbCl_6 \cdot n$APA. Further

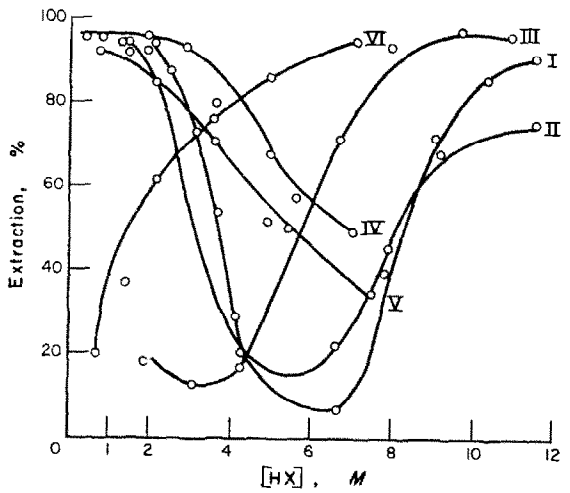

FIG. 3.—Effect of hydrohalic acid concentration on extraction of antimony(V)
PEHPA—I, HCl; IV, HBr
MEHPA—II, HCl; V, HBr
DEHPA—III, HCl; VI, HBr

work is being undertaken on the composition of these species. The change in the mechanism of extraction is also shown by the fact that in APA extractions halides can act as salting-out agents. Thus the distribution coefficient for gallium in extration from 1*M* hydrochloric acid with DEHPA can be increased from 0·07 to more than 100 by saturating the solution with calcium chloride. A further

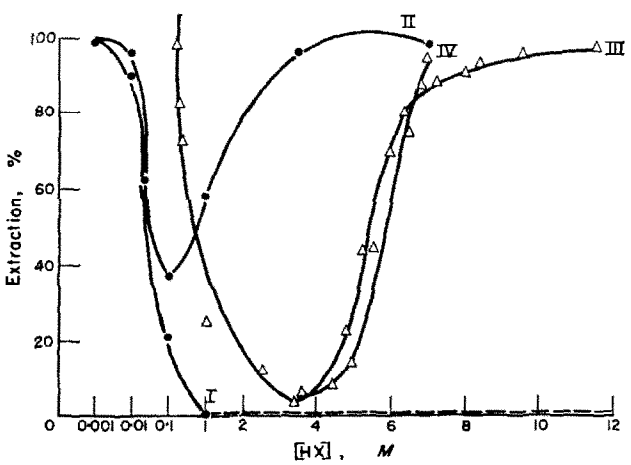

FIG. 4.—Effect of hydrohalic acid concentration on extraction of gallium and thallium with DEHPA.
I and III—HCl; II and IV—HBr
●—Tl(III); △—Ga.

indication of the change in mechanism is provided by the infrared absorption spectra. When gallium is extracted with DEHPA at pH ~ 2, the spectrum of the extract shows a considerable decrease in the intensity in the range of hydroxyl stretching modes

(2550–2700 cm^{-1}), caused by replacement of the hydrogen by metal.[6–8] When the extraction is made from concentrated hydrochloric acid solutions, the intensity of the 2550–2700 cm^{-1} band does not change but there is a sharp drop in the intensity of the band which has a maximum at 1240 cm^{-1}, corresponding to the P=O vibration. Similar changes are observed for the extraction of antimony(V) from concentrated hydrochloric acid solutions (Fig. 5). It should be noted that for extraction of gallium and antimony(V) with tributylphosphate from hydrochloric acid there is only a 70–80 cm^{-1} shift of the P=O band (Fig. 6) whereas the spectra of the DEHPA extracts show a considerable decrease in intensity as well as a shift that may be as small as 10–20 cm^{-1}.

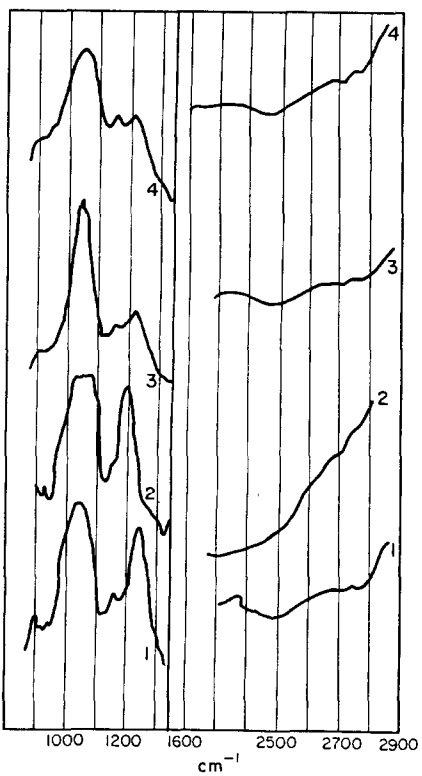

FIG. 5.—Infrared spectra of extracts *1*—DEHPA; *2*—Ga–DEHPA (from HCl, pH 2); *3*—Ga–DEHPA (from conc. HCl); *4*—Sb(V)–DEHPA (from conc. HCl).

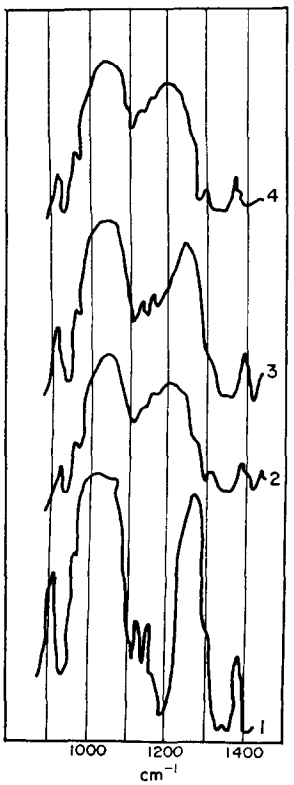

FIG. 6.—Infrared spectra of extracts *1*—TBP; *2*—HCl; *3*—Ga; *4*—Sb(V).

Antisynergic stripping

Antisynergism is manifested in APA systems by the reduction in the extracting ability of these reagents by addition of other solvents, especially alcohols, ketones and trialkylphosphates,[9–21] and is apparently caused by interaction between the components of the mixed extractant, according to the equation

$$xS + y(APA)_n \rightarrow ky(APA)_m \cdot xS$$

where S represents the second solvent and $m = n/k$. The degree of association (n)

of the APA depends on such factors as the nature of the diluent and the presence of moisture.

The utilization of antisynergism not only facilitates stripping, but also extends the range of stripping agents available, so that the most convenient one for a particular purpose can be selected. A typical example is shown in Fig. 7. Strictly speaking, all diluents can be regarded as potential antisynergic agents, but there is no universal comprehensive explanation so far of their influence on extraction with APA. To explain it entirely in terms of dielectric constants, dipole moments, polarizability, *etc.*, is to oversimplify the problem. This is clearly shown by the data summarized in Table I.

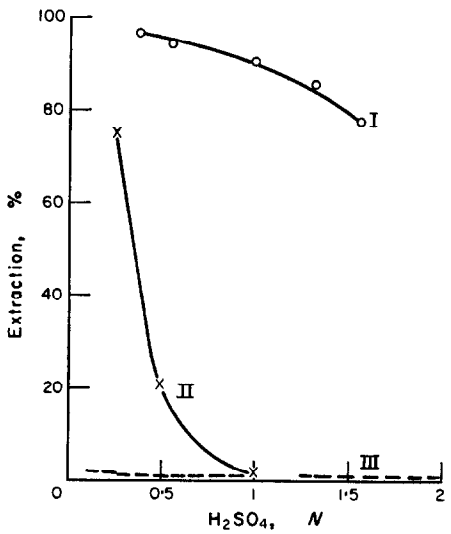

FIG. 7.—Antisynergic effect in the system MEHPA—TBP—H_2SO_4—Bi.
I—Bi—MEHPA; [Bi] 1 g/l.; [MEHPA] 0·25*N*
II—Bi-MEHPA-TBP; [MEHPA] 0·25*N*; [TBP] 1·25*N*
III—Bi-TBP; [TBP] 3·76*N*.

It seems to us that the decisive factor is hydrogen bonding between the APA and the diluent. It leads to depolymerization of the extracting agent, resulting in a greater accessibility of hydrogen ions to the cations being extracted. The influence of the nature of these cations is being studied.

SEPARATION METHODS

Indium

Indium can be extracted from 1–2*N* sulphuric, nitric or perchloric acid solution with a 1*N* solution of mono-, di- or pyro-2-ethylhexylphosphoric acid (or a similar APA) in a saturated hydrocarbon. Feebly extracted impurities such as copper, zinc and cadmium remain in the aqueous phase after scrubbing. Gallium, thallium, antimony, bismuth, tin, titanium, zirconium, hafnium, scandium, uranium, thorium, and molybdenum are extracted along with the indium. Gallium, however, is not extracted if DEHPA is used. Iron(III) must be reduced before the extraction. Antimony and bismuth are stripped with an oxalic acid solution, but if bismuth is present

in large amounts it can be stripped with potassium iodide solution. The indium is then stripped with hydrochloric or hydrobromic acid or by addition of an antisynergic agent and extraction with an oxygen acid (sulphuric is best). The other elements are either not stripped or do not interfere if the indium is then determined with Rhodamine 6 G.

TABLE I.—INFLUENCE OF DILUENTS ON THE EXTRACTION OF INDIUM WITH MEHPA AND DEHPA

DEHPA				MEHPA			
Diluent	ε	μ	D	Diluent	ε	μ	D
Iso-octane	1·94		6·6	Carbon			
Bromoform	10·36	2·06	0·63	tetrachloride	2·238	0	9·3
Benzene	2·284	0	0·63	Benzene	2·284	0	8·5
Carbon				Heptane	1·924		7·7
tetrachloride	2·238	0	0·51	Bromobenzene	10·36	1·73	5·7
Dichloroethane	5·4	1·23	0·4	Nitrobenzene	34·82	3·99	1·1
Nitrobenzene	34·82	2·99	0·4	Dibutyl ether	3·06	1·22	0·63
Dibutyl ether	3·06	1·22	0·34	Isoamyl acetate	4·63	1·8	0·09
Isobutanol	17·7	1·79	0·02	Isobutanol	17·7	1·79	0·03
				TBP			0·001

ε—dielectric constant; μ—dipole moment; D—distribution coefficient; 0·01M indium, 1·5N sulphuric acid.

Antimony

Antimony(III) can be extracted from 1–4N sulphuric, nitric or perchloric acid with a 1N solution of mono-, di- or pyroalkylphosphoric acid in a saturated hydrocarbon. Feebly extracted species such as copper and zinc remain in the aqueous phase after scrubbing with 1–2N sulphuric acid. Thallium and bismuth are stripped with a halide solution and then antimony(III) is stripped with hydrochloric, hydrobromic or oxalic acid, or by adding an antisynergic agent and an oxy-acid. The choice of stripping agent is determined by the other elements present in the extract. The expediency of extracting antimony(V) from concentrated hydrochloric or hydrobromic acid is being examined.

Bismuth

Bismuth can be extracted from 1–6N sulphuric acid with a freshly diluted or stabilized[22] 1N solution of pyroalkylphosphoric acid in a saturated hydrocarbon. The organic phase is scrubbed with 1–2N sulphuric acid to free it from feebly extracted species such as zinc and cadmium *etc.* Bismuth is stripped with a hydrohalic acid, oxalic acid, halide, or ammonium oxalate solution, the best choice being potassium iodide solution, as the bismuth can then be determined colorimetrically in the aqueous phase.

Zusammenfassung—Die Verwendung von Alkylphosphorsäuren zu extraktiven Trennungen wird beschrieben und der Gebrauch antisynergischer Agentien zur Rückextraktion diskutiert.

Résumé—On décrit l'emploi d'acides alkylphosphoriques pour les séparations par extraction par solvant et discute de l'emploi d'agents antisynergiques pour les réextractions.

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APDC-MIBK EXTRACTION SYSTEM FOR THE DETERMINATION OF TRACE ELEMENTS IN SALINE WATERS BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY*

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Summary—A technique has been developed for the determination of "soluble" cobalt, copper, iron, lead, nickel and zinc in saline waters by simultaneous extraction of their complexes with ammonium pyrollidine dithiocarbamate (APDC) into methyl isobutyl ketone (MIBK) and subsequent analysis by atomic-absorption spectrophotometry. Particulate matter is analysed separately by dissolving millipore filters in an acetone–hydrochloric acid mixture. Various analytical and instrumental parameters have been evaluated. The method is self-compensating in that it makes allowance for any incomplete extraction of the complexes. The technique has been applied to the determination of these elements in sea-water and saline lakes.

IN RECENT years, the determination of trace elements in sea-water has received increasing attention and the use of modern instrumental methods is beginning to produce significant success in this field. Riley[1] has summarized available data and it would appear that neutron activation, isotope dilution and atomic-absorption spectrophotometry may offer the best hope for reliable analyses of trace constituents in sea-water.

In 1962, Fabricand *et al.*[2] used direct aspiration of raw sea-water for the determination of trace elements by the atomic-absorption technique. Their work does not appear to have been repeated by other workers for the elements studied and because of scattering effects and clogging of the burner it is difficult to understand how they could have obtained the sensitivities and reproducibilities claimed under the conditions used.

Recently, Sprague and Slavin[3] have shown that a number of elements may be separated from 25% potassium chloride solutions by extraction of their complexes with ammonium pyrollidine dithiocarbamate (APDC) into methyl isobutyl ketone (MIBK). They have suggested use of this system for the determination of trace elements in sea-water. In an earlier paper,[4] Brooks *et al.* explored the potentialities of this system for the determination of copper in sea-water and developed a self-compensating method in which incomplete extraction of the copper complex was corrected for by extracting the standards from previously-extracted sea water.

The purpose of this publication is to describe a modification of that method, in which the scope of the technique is extended to cover the determination of cobalt, iron, lead, nickel and zinc as well as copper. A number of sea-water samples have been analysed for all these elements both in the "dissolved" and particulate fractions. The method is rapid and simple, and essentially involves the use of only two reagents, both of which can be easily purified.

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EXPERIMENTAL

Apparatus

Atomic-absorption measurements were carried out on a Perkin Elmer 303 Atomic Absorption Spectrophotometer equipped with a standard burner for use with air–acetylene. The output of the instrument was connected to a Sargent Model MR recorder *via* a Perkin Elmer Recorder Readout Accessory. Standard hollow cathode lamps were used for all elements except cobalt, for which a "High-Brightness" lamp was used.

Reagents

Redistilled reagent-grade hydrochloric acid, 6*N*.

Redistilled commercial-grade methyl isobutyl ketone.

A 1% aqueous solution of APDC (Eastman Chemicals). The solution, which was prepared daily, was purified by shaking with an equal volume of MIBK, separating the phases and filtering the lower aqueous phase. Since APDC is only slightly soluble in MIBK whereas metal complexes are very soluble, the reagent is easily purified in this manner.

A standard aqueous solution (pH 4) containing 40 ppm each of cobalt, copper, iron, lead, nickel and zinc.

Distribution coefficients of the metal complexes between sea-water and MIBK

The method is dependent on the use of large sea-water/solvent ratios in order to achieve a concentration effect as well as separation from bulk constituents. The degree of extraction will decrease as the volume ratio increases since the relationship between the distribution coefficient (D), the degree of extraction (E) and the volumes of the organic phase (V_o) and aqueous phase (V_a) is given by the expression:

$$E = \frac{100D}{D + V_a/V_o} \%.$$

This relationship is illustrated graphically in Fig. 1. It will be noted that it is essential to have some indication of the value of the distribution coefficient before deciding what sea-water/solvent ratio to use. For example, doubling the volume ratio from 50 to 100 will increase the concentration in the organic phase by 91% for a complex with a value of $D = 1000$, 82% for $D = 500$, 50% for $D = 100$, 33% for $D = 50$ and only 9% for $D = 10$. Little increase in sensitivity would therefore be gained for the less-strongly extracted elements by changing the phase ratio. Figure 1 has been presented so that others working with this method may choose their own volume ratios, but in the following study a ratio of 750:20 was used.

Approximate distribution coefficients for the elements were determined by analysis of successive extracts from sea-water spiked with 5 ppm quantities of the ions concerned. Provided that D is greater than 10, the ratio of the concentrations in any two successive extracts is an approximate measure of the distribution coefficient. These values obtained are shown in Table I.

Stability of the complexes

The stability of the complexes was measured by preparing APDC extracts in MIBK and comparing the absorbance of these with stable solutions in dilute acid. All complexes were stable for several hours. The minimum times for which no appreciable loss of absorbance was noted are also shown in Table I. It is clear that provided that all samples are analysed within 3 hr of extraction, no difficulty should be encountered. The extracts may be preserved for considerably longer periods by freezing in acetone–dry ice or liquid nitrogen. It is also possible to prolong storage by freezing as before, allowing the extract to warm until the MIBK has melted, and then decanting off the organic layer from the small bead of ice which forms at the bottom of the container.

The determination of "soluble" cobalt, copper, iron, lead, nickel and zinc in sea-water

The following technique was developed to fully compensate for any incomplete extraction of the elements with a sea-water/solvent ratio of 750:20 and was carried out on the "soluble" ions present in sea-water that had been filtered through a 0·45 μ millipore.

Sufficient redistilled hydrochloric acid was added to the filtered sea-water to adjust the pH to between 4 and 5. This step is only necessary if the water is to be stored for some time before use and is a precautionary measure to lessen the danger of adsorption or precipitation of colloidal material on the walls of the container. Extraction can be carried out equally well at the pH of sea-water (8) and the authors have noted experimentally that a dilute suspension of iron(III) hydroxide will gradually dissolve in APDC at this pH though equilibrium is likely to be reached faster at the lower pH. Great

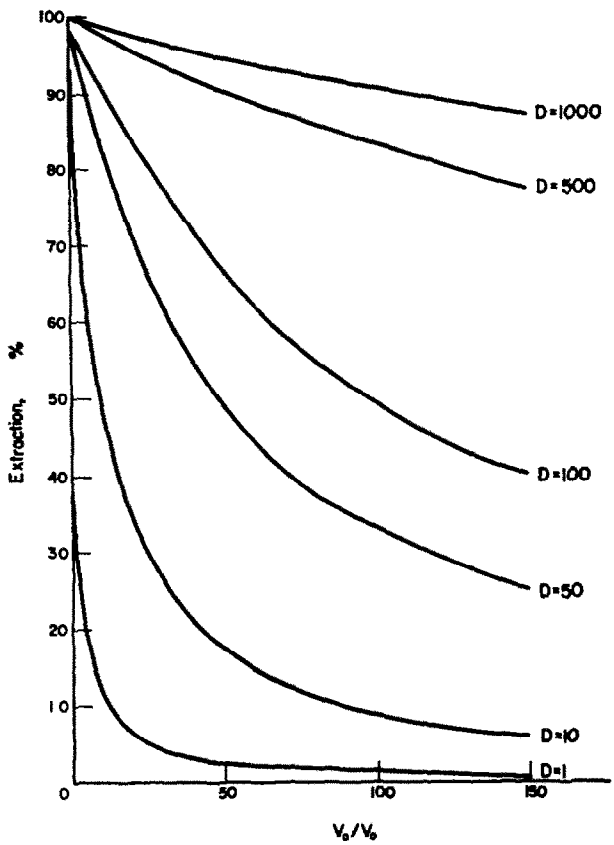

FIG. 1.—Degree of extraction as a function of phase ratios for different values of the distribution coefficient (*D*).
V_a—Volume of aqueous phase
V_o—Volume of organic phase.

TABLE I.—ANALYTICAL AND INSTRUMENTAL PARAMETERS

Parameter	Co	Cu	Fe	Ni	Pb	Zn
Distribution coefficient of APDC complex between MIBK and sea-water at pH 3·5	~600	~600	~300	~350	~500	~100
Minimum time for which complex is stable, *hr*	24	24	3	3	5	5
Coefficient of variation for replicate analyses (%)	15	4	6	11	8	3
Instrumental scale-expansion	× 10	× 10	× 10	× 10	× 10	× 3
Instrumental noise-suppression	4	3	4	4	4	3
Analysis line, *mμ*	241	325	248	232	317	214
Approximate limits of detection, *ppb*	0·10	0·10	0·10	0·10	0·20	0·05

care must be taken to ensure that the pH of the sea water does not fall below 3·5 as our investigations have shown that extraction of zinc decreases rapidly below this pH and ceases completely at a pH of about 2·5.

Samples of sea-water (750 ml) were placed in 1000-ml polypropylene Erlenmeyer flasks (glassware has been used successfully but polypropylene is considered more satisfactory as there is less danger from contamination or adsorption effects) and 35 ml of MIBK were added to each flask followed by 7 ml of 1% APDC solution. The samples were then equilibrated for 30 min on a mechanical shaker. The phases were separated by means of a separatory-funnel and the organic phases were stored in polypropylene bottles.

In order to prepare a working curve, a further 20 ml of MIBK were added to each sample of extracted sea-water and the phases were separated after a further 5 min equilibration. The purpose of this operation was to ensure that the sea-water was as free as possible from the trace elements under

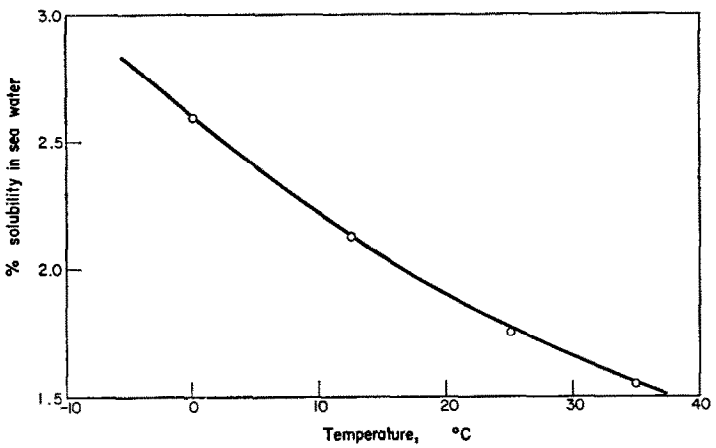

FIG. 2.—Solubility of MIBK in sea-water as a function of temperature.

investigation. The sea-water samples were then recombined to ensure homogeneity and eight 750-ml samples were replaced in the flasks. Incremental amounts of the six elements were then added to give concentrations of 0, 2, 5 and 10 ppb* in the sea-water. The temperature of the water was measured and the volume of MIBK remaining after the first equilibration (approx 20 ml) was calculated from the authors' data on the solubility of this solvent in sea-water (see Fig. 2). This volume of MIBK and 7 ml of APDC solution were then added to the contents of each flask. Shaking for 30 min and phase separations were carried out as before.

The samples were then aspirated into a fuel-lean air–acetylene flame under the working conditions shown in Table I. Typical working curves are shown in Fig. 3.

A number of sea-water samples (salinity 3·5%) were analysed by the method and the results are summarized in Table II. Results for Lake Abert, Oregon (salinity 31·6%) and interstitial water from sediment of the Dead Sea (salinity 31·0%) were also obtained.

The precision of the method

The precision of the method was tested by replicate analyses on twelve identical samples of sea-water. The coefficients of variation are shown in Table I and are applicable for concentrations of 1 ppb of cobalt, 3 ppb of copper, 12 ppb of iron, 5 ppb of lead, 2 ppb of nickel and 1 ppb of zinc.

The preparation of the blank

Since extremely small quantities of trace elements are involved in these studies, extreme care must be taken in preparing the blank. The zero of the working curve is usually sufficient for this purpose. It does not however take account of the amount of MIBK which dissolved in the sea-water or the acid which is sometimes used to reduce the pH. It was found that if the MIBK was evaporated down to the volume of it normally left after extraction with sea-water, the atomic-absorbance of this "concentrated" solvent was exactly the same as that of the original material for all six elements. It is not

* *i.e.*, 1 in 10^9.

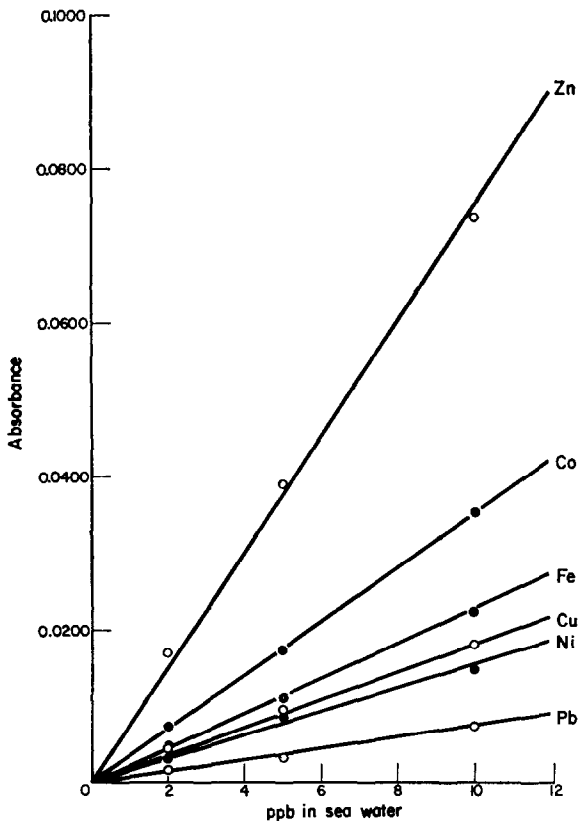

FIG. 3.—Working curves for various elements.

therefore our practice to make a blank correction for the MIBK itself having once ensured that a particular batch is free from contamination.

If a blank correction is made for the acid however, anomalous results can sometimes occur, possibly because of a compositional effect which becomes evident at high scale-expansions. The best procedure to follow in such cases is either not to use acid at all in the analytical procedure or else to check that the acid used is free from contamination, by analysing it by direct aspiration, and then not to use it in the determination of the blank correction.

The determination of particulate cobalt, copper, iron, lead, nickel and zinc

A simple technique has been developed for the simultaneous determination of these elements in the particulate matter of sea-water.

After passage of 1000 ml of sea-water through a 0·45-μ millipore filter, the filter was washed with 50 ml of distilled water and placed in a polypropylene bottle. Five ml of redistilled 6*M* hydrochloric acid were added to each sample and the bottles were sealed and maintained at 70° for 1 hr; then 15 ml of acetone were added to each sample to dissolve the millipore and to form a single phase. Addition of a threefold amount of acetone served rather to enhance absorption than to reduce it, in spite of the dilution effect. This is because of the "solvent effect" in atomic-absorption spectrophotometry[5] (which is also utilized in the MIBK extraction method to give a threefold absorption enhancement compared with aqueous solutions). The effect of adding acetone is demonstrated in Fig. 4 and is particularly important in this work as it provides a sufficient sample volume for the determination of six elements simultaneously.

The samples were analysed against standards prepared in a similar matrix and the results are shown in Table II.

TABLE II.—TRACE ELEMENTS IN SALINE WATERS
(Concentration, *ppb*)

Type of water	Depth, *m*	Location	Co		Cu		Fe		Ni		Pb		Zn	
			A	B	A	B	A	B	A	B	A	B	A	B
Ocean	Surface	S. Calif. Coast 1 mile SW San Pedro	1.1	<0.1	3.0	1.3	11.7	32.6	2.5	<0.1	5.2	13.0	0.8	2.1
Ocean	Surface	S. Calif. Coast 10 miles SW San Pedro	1.2	<0.1	2.8	0.2	10.8	3.8	1.5	<0.1	3.8	1.4	13.8	0.3
Ocean	Surface	S. Calif. Coast 22 miles SW San Pedro	0.3	<0.1	1.3	0.3	1.3	5.0	1.6	<0.1	2.6	1.6	3.4	0.5
Ocean	Surface	S. Calif. Coast 38 miles SW San Pedro	0.1	<0.1	1.7	0.5	0.6	1.3	1.0	<0.1	<0.2	0.4	0.4	0.7
Ocean	300	S. Calif. Coast 38 miles SW San Pedro	0.2	<0.1	6.6	1.6	3.2	37.4	1.7	<0.1	1.8	4.0	28.2	13.0
Ocean	600	S. Calif. Coast 38 miles SW San Pedro	0.2	<0.1	4.0	0.9	1.8	6.5	0.9	<0.1	4.2	1.7	16.4	2.0
Ocean	750	S. Calif. Coast 38 miles SW San Pedro	0.1	<0.1	4.8	0.6	2.5	11.0	0.9	<0.1	4.0	0.7	22.0	2.2
Ocean	900	S. Calif. Coast 38 miles SW San Pedro	<0.1	<0.1	1.9	0.6	0.9	4.4	0.4	<0.1	2.3	1.8	4.8	3.0
Ocean	1050	S. Calif. Coast 38 miles SW San Pedro	0.1	<0.1	2.6	6.4	1.1	4.4	0.8	<0.1	1.2	2.6	6.4	1.6
Lake	Surface	L. Abert, Oregon	0.4	n.d.	4.8	n.d.	0.1	n.d.	2.0	n.d.	3.8	n.d.	3.2	n.d.
Lake	330	Dead Sea, Israel	8.4	n.d.	1.2	n.d.	86.4	n.d.	57.0	n.d.	28.2	n.d.	288.0	n.d.

A—"Soluble" fraction.
B—Particulate fraction.
n.d.—Not determined.

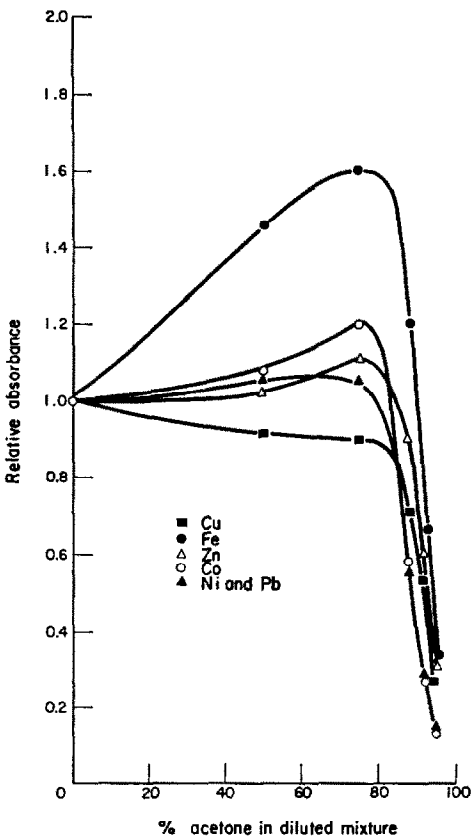

FIG. 4.—Effect of dilution with acetone on the relative absorbance of an initially aqueous solution.

RESULTS AND DISCUSSION

With the exception of lead, the "soluble" and particulate values for the various elements fall within the expected limits. The fact that particulate values are higher than the "soluble" figures for iron and lead and lower for copper and zinc, conforms to the expected pattern.

Values for "soluble" cobalt, iron, lead and nickel show a steady decrease as the sampling points move progressively further away from the coast. The values for lead are particularly striking and are probably due to excessive atmospheric pollution above the Los Angeles Basin as well as to sewage effluent.

It is concluded that the advantages of the method lie in its speed, relative freedom from contamination effects, relatively good precision, high sensitivity (limits of detection are shown in Table I) and the self-compensation for any incomplete extraction of the ions concerned. For this last reason, it has not been necessary to carry out the usual addition and recovery experiments which are conventionally applied to a new technique. The method is now being used for further analyses of sea-water and the interstitial waters of ocean sediments.

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Zusammenfassung—Ein Verfahren wurde für die Bestimmung von "löslichem" Kobalt, Kupfer, Eisen, Blei, Nickel und Zink in salzhaltigen Wassern entwickelt. Es bestand aus der Extraktion des Komplexes mit Ammoniumpyrollindithiocarbamat (APDC) und Methylisobutylketon (MIBK) mit anschliessender Bestimmung mit Flammenabsorptionsspektroskopie. Unlösliche Bestandteile wurden bei direkter Lösung des Filters in einer Azeton–Salzsäuremischung bestimmt. Verschiedene analytische und instrumentalische Parameter wurden festgestellt und das Verfahren enthält Selbstkompensation fur unvollständige Extraktion. Die Methode wurde verwendet um diese Elemente in Seewasser und salzhaltigen Seen zu bestimmen.

Résumé—On a developpé une méthode pour le dosage de cobalt, cuivre, fer, plomb, nickel et zinc "solubles" en eaux salinaires. On a extrait le complexe avec du pyrollidine-dithiocarbamate (APDC) d'ammonium en solution de méthylisobutylcétone (MIBK) et effectué la détermination finale par spectrophotométrie par absorption atomique. On a dosé les constituants insolubles par dissolution du filtre dans un melange d'acétone et d'acide chlorhydrique. On a évalué plusieurs parametres analytiques et instrumentaux et la méthode possède une compensation interne pour l'extraction incomplète. On a utilisé la méthode pour le dosage de ces elements dans l'eau de mer et lacs salinaires.

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RADIOCHEMISCHE TRENNUNGEN MIT HILFE DER RINGOFENMETHODE—II

DAS SYSTEM $^{99}Mo/^{99m}Tc$

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Zusammenfassung—^{99}Mo-^{99m}Tc-Trennungen lassen sich unter Anwendung der Ringofenmethode durchführen. Am besten gelingt die Trennung auf Rundfiltern, welche mit Berliner Blau oder Mangandioxid imprägniert sind. Hierbei bleibt Molybdän im Zentrum des Rundfilters fixiert, während Technetium mit 70 bis über 90% Ausbeute im Ring konzentriert wird. Die Dekontaminationsfaktoren erreichen Werte von $\geqslant 10^3$. Ist nach einer Trennung wieder genügend ^{99m}Tc nachgebildet, so kann es erneut vom Mutternuklid "abgemolken" werden. Die Halbwertszeit des abgetrennten ^{99m}Tc wurde zu 6,06 ± 0,05 Std. ermittelt.

KÜRZLICH wurde am Beispiel des Mutter-Tochter-Paares $^{137}Cs/^{137m}Ba$ gezeigt, wie sich die Ringofenmethode nach Weisz für einfach und schnell auszuführende radiochemische Trennungen heranziehen läßt.[1] Die Trennoperationen wurden auf Rundfiltern vorgenommen, welche mit anorganischen Ionenaustauschern imprägniert waren. Hierbei blieb das ^{137}Cs in der Mitte des Rundfilters fixiert, während das ^{137m}Ba vom Mutternuklid "abgemolken" und in einer scharfen Ringzone von 22 mm Durchmesser wieder konzentriert werden konnte.

Im folgenden wird gezeigt, wie man nach dem gleichen Prinzip in 2–2½ min ^{99m}Tc von ^{99}Mo abtrennen kann. Zur Durchführung dieser Trennung war es notwendig, geeignete Sorbentien für Molybdän zu finden und die 5·5 cm-Rundfilter damit zu imprägnieren. Von allen getesteten Imprägnierungen wurden schließlich nur vier eingehender untersucht, nämlich Berliner Blau, Mangandioxid, Zirkoniumphosphat und Aluminiumoxid.

Die Verwendung von Aluminiumoxid als Säulenmaterial für ^{99m}Tc-Generatoren wurde verschiedentlich beschrieben.[2,3] Z. Kolařik und J. Krtil[4] untersuchten die Sorption einiger Spaltprodukte an Mangandioxid-Säulen. Die Ionenaustauscheigenschaften von Zirkoniumphosphat[5–11] sowie deren Ausnutzung für radiochemische Trennungen[12–16] waren Gegenstand eingehender Untersuchungen.

EXPERIMENTELLER TEIL

Filtermaterialien

Berliner Blau-Papiere. Die Imprägnierung von Rundfiltern mit Berliner Blau wurde bereits beschrieben.[1] Die Papiere wurden teilweise lufttrocken verwendet, zum Teil jedoch vor Gebrauch 10 min bei 110° im Trockenschrank getrocknet.

Mangandioxid-Papiere. Rundfilter MN 2260 von 5,5 cm Durchmesser (Hersteller: Macherey, Nagel u. Co., Düren) wurden mit einer 1,5%igen $KMnO_4$-Lösung getränkt und auf Filterpapier abgepreßt. Anschließend tauchte man jeweils 5 Papiere 15–30 sec in 100 ml einer 3%igen H_2O_2-Lösung, preßte sie wiederum ab und legte sie *ca.* 1 Std. in dest. Wasser, wobei dieses alle 10 min erneuert wurde.

Zum Schluß wurden die Rundfilter mit dest. Wasser abgespült und auf Filterpapier an der Luft getrocknet. Nach der Imprägnierung von je 5 Rundfiltern wurde die H_2O_2-Lösung erneuert.

Zirkoniumphosphat-Papiere. Rundfilter MN 2260 wurden mit einer $ZrOCl_2$-Lösung, welche 2%ig in Bezug auf Zr(IV) ist, getränkt, auf Filterpapier abgepreßt, 15–30 sec in 1%iger Phosphorsäure gebadet und wiederum abgepreßt. Anschließend wässerte und trocknete man die Papiere wie oben.

Aluminiumoxid-Papiere. Es wurden 5,5 cm-Rundfilter aus Bögen des Aluminiumoxid-Papiers Nr. 288 der Fa. Schleicher und Schüll (Dassel/Kr. Einbeck) ausgeschnitten.

Meßgeräte

Gammaspektren wurden mit einem Harshaw-NaJ (Tl)-Kristall (2 in. × 2 in.; 8 S 8/EP) sowie einem 100 Kanal-Impulshöhenanalysator der Fa. Technical Measurement Corp., North Haven, (Gammascope II/Modell 102) aufgenommen. Die zur Ermittlung der Halbwertszeit des abgetrennten ^{99m}Tc notwendigen Messungen erfolgten mit einem FH 421/Z4-NaJ(Tl)-Kristall sowie einem FH 49-Zählgerät der Fa. Frieseke u. Hoepfner, Erlangen-Bruck.

Durchführung der Versuche

Eine alkalische $Na_2{}^{99}MoO_4$-Lösung mit einer spez. Aktivität von etwa 140 μC/ml und einer Trägermenge von rund 0,2 mg Mo(VI)/ml stand zur Verfügung. Hiervon wurden 0,6 ml mit 4 Tropfen 65%iger Salpetersäure angesäuert und 5 μl der so erhaltenen Probelösung im Zentrum eines imprägnierten Rundfilters aufgetragen. (Auf dem Filter befanden sich somit *ca.* 0,5 μC ^{99}Mo mit 0,75 μg Mo(VI)-Träger). Nach dem Trocknen wurde auf dem Ringofen mit 80–120 μl 0,05n Salpetersäure oder 120–150 μl 50% äthanolischer 0,05n Salpetersäure das ^{99m}Tc aus dem zentralen Mo(VI)-Tüpfelfleck abgetrennt und im Ring konzentriert. Diese Trennung ließ sich in 2–2½ min ausführen. Anschließend wurde das Rundfilter getrocknet und aus dem Zentrum desselben ein Scheibchen von 17 mm Durchmesser (mit dem Mo(VI)-Tüpfelfleck in der Mitte) herausgeschnitten vgl. 1. Mitteilung[1]). Das Scheibchen (^{99}Mo) und das restliche Filter mit dem im Ring konzentrierten ^{99m}Tc gelangten unmittelbar danach zur Aktivitätsmessung.

Es konnte 22–24 Std. (~4 Halbwertszeiten von ^{99m}Tc) nach der ersten Trennung aus dem 17 mm-Scheibchen mit dem Mo(VI)-Tüpfelfleck erneut ^{99m}Tc "abgemolken" werden. Hierzu wurde das Filterscheibchen auf die mitte eines neuen imprägnierten Rundfilters gepreßt[1,17] und das ^{99m}Tc mit 120–150 μl wsäsriger 0,05n Salpetersäure oder rund 200 μl 50% äthanolischer 0,05n Salpetersäure in die Ringzone gewaschen. Hierbei gingen bis zu 10% des ^{99}Mo aus dem Filterscheibchen mit in das untere Rundfilter über, sodaß vor Beginn der Messungen aus dessen Zentrum ein Scheibchen von 18 mm Durchmesser (mit der störenden ^{99}Mo-Aktivität) ausgeschnitten werden mußte (vgl. 1. Mitteilung[1]).

ERGEBNISSE UND DISKUSSION

Die nach jeder Trennung aufgenommenen γ-Spektren vom 17 mm-Scheibchen und Ring dienten zur Bestimmung der ^{99m}Tc-Ausbeute und der radiochemischen Reinheit des abgetrennten Tochternuklids. Die Ausbeute wurde an Hand des 0,14 MeV-Peaks von ^{99m}Tc, der Dekontaminationsfaktor mit Hilfe des 0,74/0,78 MeV-Peaks von ^{99}Mo ermittelt. Abbildung 1 zeigt die nach einer Trennung auf Berliner Blau-Papier (mit 0,05n Salpetersäure) gemessenen γ-Spektren von Scheibchen und Ring im Bereich der 0,38 MeV- und 0,74/0,78 MeV-Peaks von ^{99}Mo.

Beim Vergleich der zwei verwendeten Waschflüssigkeiten (äthanolische bzw. wässrige 0,05n Salpetersäure) ergab sich, daß man für das abgetrennte ^{99m}Tc mit ersterer die niedrigsten, mit letzterer die höchsten Dekontaminationsfaktoren erzielt.

Hinsichtlich der Ausbeuten ließen sich nur bei Verwendung von Aluminiumoxid-Papieren merkliche Unterschiede zwischen den zwei Waschflüssigkeiten feststellen: hier lieferte wässrige 0,05n Salpetersäure die geringsten ^{99m}Tc-Ausbeuten. Trocknete man die Berliner Blau-Papiere vor Gebrauch 10 min bei 110°, so bewirkte dies eine deutliche Steigerung der ^{99m}Tc-Ausbeute. Ähnliche Veränderungen in den Ionenaustauscheigenschaften in Abhängigkeit von der Trocknungstemperatur wurden für Zirkoniumphosphat beschrieben.[16,18]

Beim Vergleich der vier untersuchten Papiersorten liess sich folgendes feststellen: beim Arbeiten mit wässriger 0,05n Salpetersäure als Waschflüssigkeit und unter Verwendung einer frisch angesäuerten $^{99}MoO_4^{2-}$-Lösung wurden auf Zirkoniumphosphat-, Berliner Blau- und Mangandioxid-Papier ^{99m}Tc-Ausbeuten von 70 bis über 90% erreicht. Lediglich das Aluminiumoxid-Papier lieferte Ausbeuten von 50–60%. Beim "Abmelken" aus den 17 mm-Scheibchen fielen diese Werte unterschiedlich ab, am wenigsten bei Trennungen auf Mangandioxid-Papieren, besonders

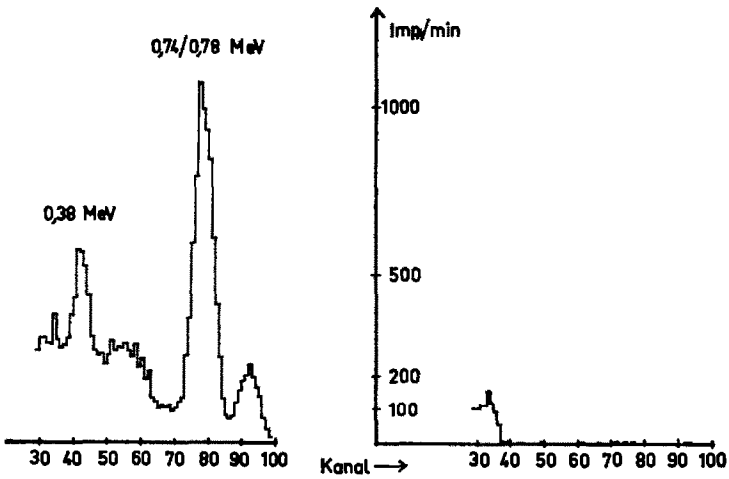

Abb. 1.—Gammaspektren von ^{99}Mo.
(*a*) Im Zentrum von 17 mmϕ.
(*b*) Im äusseren Ring.

stark bei Trennungen auf Aluminiumoxid-Papieren. Mehrere Versuchsreihen ergaben, daß man die radiochemisch reinsten ^{99m}Tc-Präparate dann erhält, wenn man Berliner Blau- oder Mangandioxid-Papiere verwendet. Mit wässriger 0,05n Salpetersäure als Waschflüssigkeit wurden hier stets Dekontaminationsfaktoren $> 10^3$ erreicht, während auf Zirkoniumphosphat- und Aluminiumoxid-Papieren häufig nur kleinere Werte erzielt werden konnten.

Zusammenfassend konnte festgestellt werden, daß hinsichtlich Ausbeuten und Dekontaminationsfaktoren optimale ^{99}Mo-^{99m}Tc-Trennungen auf Berliner Blau-Papieren (bei 110° getrocknet) sowie Mangandioxid-Papieren unter Verwendung einer salpetersauren Probelösung und von wässriger 0,05n Salpetersäure als Waschflüssigkeit auszuführen sind.

Wie bereits angedeutet, werden die obengenannten Ausbeuten nur in den ersten Stunden nach dem Ansäuern der alkalischen $^{99}MoO_4^{2-}$-Lösung mit Salpetersäure erreicht. Je länger die Zeitspanne zwischen Ansäuern und Durchführung einer Trennung ist, desto mehr gehen die ^{99m}Tc-Ausbeuten zurück, und zwar bei allen hier verwendeten Adsorbentien. Inwiefern dabei ein Wechsel der Oxydationsstufe des Technetiums eine Rolle spielt (vgl. bei R. Münze[19]), muß noch untersucht werden. In mehreren Versuchen wurde die Zerfallskurve des abgetrennten ^{99m}Tc aufgenommen. Abbildung 2 zeigt ein Beispiel hierfür. Aus vier solchen Abfällen (Dekontaminationsfaktoren $> 10^3$) wurde die Halbwertszeit von ^{99m}Tc durch Ausgleichsrechnung zu 6,06 $\pm$ 0,05 Std. berechnet.

Bemerkenswert erscheint die Tatsache, daß von allen untersuchten Hexacyanoferraten(II) (Berliner Blau, Co-Hexacyanoferrat, Cu-Hexacyanoferrat, V(IV)-Hexacyanoferrat) lediglich Berliner Blau Molybdän(VI) in solchem Ausmaße zu sorbieren vermag, daß es für eine ^{99}Mo-^{99m}Tc-Trennung nach dem geschilderten Verfahren geeignet ist. Mangandioxid wies von allen getesteten Sorbentien die

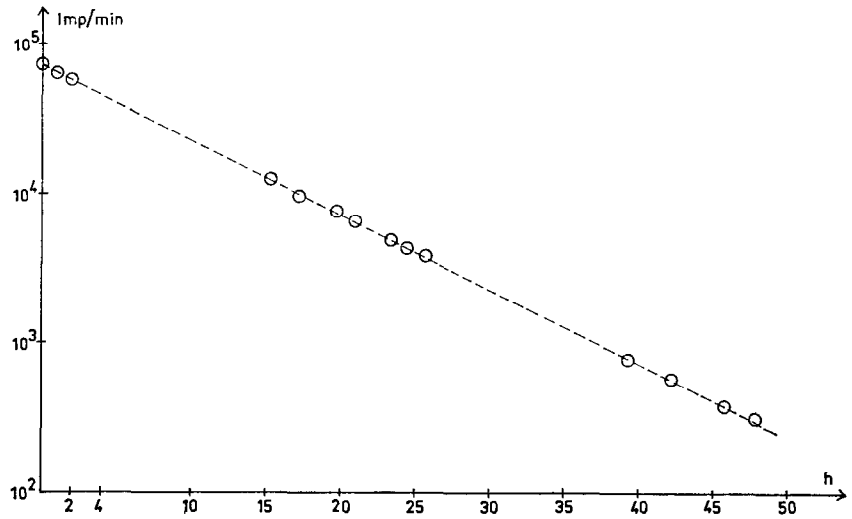

ABB. 2.—^{99m}Tc-Abfall im Ring.

geringste Stabilität gegenüber der verwendeten Waschflüssigkeit auf. Es zeigte sich eine deutliche Aufhellung im Zentrum der mit Mangandioxid imprägnierten Rundfilter nach dem Waschen mit 0,05n Salpetersäure.

Trotzdem liessen sich auf Mangandioxid-Papieren saubere Trennungen durchführen. Im Hinblick auf die Tatsache, daß ^{99m}Tc in steigendem Maße an Stelle von ^{131}J zur Markierung von Proteinen herangezogen wird,[20–22] dürften die geschilderten Eigenschaften von Berliner Blau und Mangandioxid von Interesse sein.

Herrn Prof. Dr. W. Seelmann-Eggebert, dem Direktor des Instituts für Radiochemie im Kernforschungszentrum Karlsruhe, möchte ich an dieser Stelle für die Überlassung der ^{99}Mo-Lösung herzlich danken.

Summary—The separation of ^{99}Mo and ^{99m}Tc by the ring-oven technique is described. The separation is best carried out on round papers impregnated with Prussian Blue or with manganese dioxide, when the molybdenum is fixed in the centre of the paper and the technetium is concentrated with 70–90% yield in the ring. Decontamination factors of $\geqslant 10^3$ were obtained. ^{99m}Tc formed after the separation can be further leached from the parent nuclide. The half-life of ^{99m}Tc was found to be 6·06 ± 0·05 hr.

Résumé—On décrit la séparation de ^{99}Mo et ^{99m}Tc par la technique du four annulaire. La séparation est menée au mieux sur des ronds de papier imprégnés de bleu de Prusse ou de bioxyde de manganèse, auquel cas le molybdène est fixé au centre du papier et le technécium est concentré dans l'anneau avec un rendement de 70–90%. On a obtenu des facteurs de décontamination de 10^3. Le ^{99m}Tc formé après la séparation peut être davantage lixivié du nucléide-mère. On a trouvé que la demi-vie du ^{99}Tc es de 6,06 ± 0,05 h.

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DETERMINATION OF TRACES OF CALCIUM, MAGNESIUM, IRON AND NICKEL IN ALUMINIUM SALTS BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY WITH A MICROWAVE-EXCITED SOURCE AND HOLLOW-CATHODE LAMPS

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Summary—The determination of trace amounts of calcium and magnesium in solutions containing large concentrations of aluminium salts may be accomplished by co-precipitating their hydroxides on iron(III) hydroxide, dissolving the precipitate, and extracting the 8-hydroxyquinolates of calcium and magnesium into methyl isobutyl ketone at about pH 11. The extract may be sprayed into the air-propane flame of a simple unmodulated spectrophotometer and atomic-absorption measurements for calcium and magnesium made at 4227 and 2852 Å respectively. The limits of determination correspond to 10 and 1 ppm of calcium and magnesium in solid alumina. Iron and nickel may be co-precipitated on hydrated manganese(IV) oxide and their 8-hydroxyquinolates extracted at pH 4·5. Measurements of atomic absorption for these elements at 2483 and 2320 Å respectively yield limits of determination corresponding to 10 ppm in alumina. Hollow-cathode lamps may be used for calcium, magnesium and nickel, but a simple microwave-excited discharge tube gives much better sensitivity than a hollow-cathode lamp for iron.

THE determination of trace metals in nearly pure alumina presents special problems which are not easily solved by conventional analytical techniques. This communication describes attempts made to apply the sensitivity and selectivity of atomic-absorption spectroscopy to the determination of calcium, iron, magnesium and nickel in the presence of large amounts of aluminium.

The measurement for analytical purposes of absorption of radiation by free atoms demands the production of a tenuous population of these in a gas phase. At the present time this is achieved for absorption spectrophotometry almost exclusively by spraying a finely nebulized solution into a flame and measuring the attenuation in the signal from a hollow-cathode lamp emitting the necessary resonance line of the absorbing species. For many elements this procedure is entirely satisfactory, but those which form refractory oxides in flames present special difficulties because most flames are not hot enough to promote thermal dissociation of those oxides. Aluminium is one such element. Whilst many of those compounds may be sufficiently well broken down in the hot oxygen-free nitrous oxide–acetylene flame[1] to make this determination possible for trace amounts, a very considerable problem exists when these elements form the matrix in which traces of other elements have to be determined. This was confirmed in the present study when it was found that atomic absorption signals for these trace elements could not be obtained in the presence of very large amounts of aluminium.

There are several ways of overcoming this problem. One is obviously to use very hot flames such as cyanogen[2] to break down the oxide particles, but this introduces other problems which are rather difficult to solve and the depletion of ground state spectral lines and emergence of ionic lines is marked for calcium. The background emission of fuel-rich (*i.e.*, reducing) high-temperature flames is also rather high and causes excessive detector noise even in well modulated systems.

For this reason it was decided to separate (and concentrate) the desired elements from the matrix element, aluminium, by co-precipitation and solvent extraction, and to spray the extract into the flame for absorption measurements. In this way the solid matrix of alumina which might physically sequester the otherwise volatile metal atoms is eliminated, and the desired element is concentrated. At the same time the efficiency of nebulization is increased from 10–15% for aqueous solutions to 40–60% for organic solvents, thus further increasing the sensitivity of determination.

There is no need to employ specific or even selective extracting agents since inter-element interference is scarcely observed at trace levels in atomic-absorption spectroscopy.[3] For this reason an unselective and cheap extracting agent is entirely satisfactory. 8-Hydroxyquinoline is one such reagent and has been applied extensively in this laboratory to such problems.[4,5]

Calcium and magnesium are extracted only from alkaline media and in the presence of a considerable excess of 8-hydroxyquinoline. Under these conditions aluminium is much more easily extracted than either. Consequently a preliminary separation by co-precipitation on iron(III) hydroxide[6] was used to remove these elements from the aluminium in sodium hydroxide medium. Iron(III) 8-hydroxyquinolate is not easily extracted from alkaline solution by most organic solvents and the numerous lines in the iron absorption spectrum render the determination of the two other metals rather difficult. However, iron(III) 8-hydroxyquinolate can easily be extracted into ethyl acetate from an acid solution (pH $\sim$ 4·5) containing a high concentration of sodium chloride,[7] and the solution remaining can be made alkaline and the magnesium and calcium 8-hydroxyquinolates extracted into methyl isobutyl ketone and examined by atomic-absorption spectrophotometry. Sodium chloride has a marked salting-out effect on the extraction of iron(III) 8-hydroxyquinolate and to a lesser extent enhances the extraction of the magnesium and calcium complexes. Any tendency for aluminium not to be removed by this procedure would be nullified by the effect noted by Wallace.[8]

Both calcium and magnesium form 8-hydroxyquinolates with the 6-co-ordination completed by two water molecules. Consequently it is necessary to use oxygen donor solvents such as methyl isobutyl ketone to displace the co-ordinated water molecules and/or to use a large excess of 8-hydroxyquinoline for the same purpose. In this study the latter was found to be more important, and no magnesium or calcium could be detected by atomic-absorption spectroscopy of the aqueous phases after extraction of the $CaOX_2 \cdot HOX$ and $MgOX_2 \cdot HOX$ complexes[9] with 6% ethanolic 8-hydroxyquinoline solution used in conjunction with methyl isobutyl ketone as the solvent. The addition of tri-n-butylamine or butylcellosolve was not found to be beneficial.[10] The magnesium 8-hydroxyquinolate extract was found to be perfectly stable, but the corresponding calcium complex showed a tendency to separate out as a solid phase, although it remained in solution for 20 min. Consequently no difficulty is encountered if the atomic absorption of the calcium is measured within this time, preferably before that of the magnesium.

The effect of sodium chloride concentration on the extraction of 50 μg of calcium is shown in Fig. 1a, and the effect of 8-hydroxyquinoline concentration in Fig. 1b. The extraction is quantitative at pH $\geqslant$ 11. This pH is easily maintained by the addition of sodium hydroxide.

With a sample of potassium aluminium sulphate corresponding to 1 g of Al_2O_3 it was found that successful co-precipitation of magnesium and calcium hydroxides occurred when >1 mg of iron was added to a solution of the sample made alkaline with sodium hydroxide. There is no tendency for the aluminium to co-precipitate at the pH used. When amounts of iron >4 mg were used, difficulties arose in the filtra-

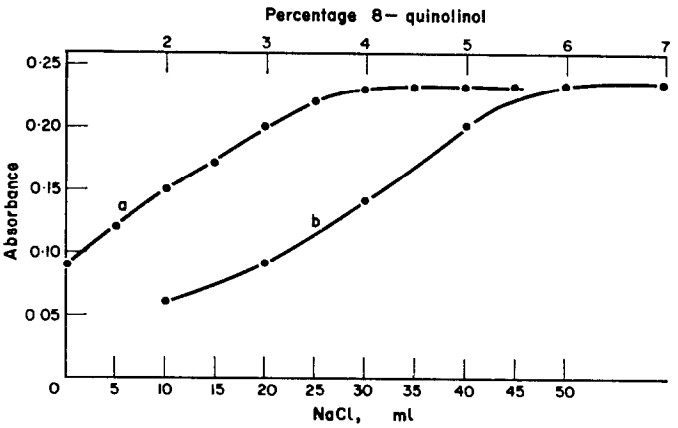

FIG. 1.—Effect of sodium chloride and 8-hydroxyquinoline concentrations on the extraction and determination of calcium.

(a) Variation of [NaCl] in solution containing 50 μg of Ca^{2+} and 2 ml of 6% 8-hydroxyquinoline solution.

(b) Variation of [8-hydroxyquinoline] in solution containing 50 μg of Ca^{2+} and 40 ml of saturated NaCl solution.

Absorbance measured in flame at 4227 Å: extraction into 10 ml of methyl isobutyl ketone.

tion and the subsequent extraction of iron, and 2 mg of iron(III) [2 ml of 0·1% solution] were therefore used as the optimal amount.

The best conditions for atomic-absorption measurements for calcium and magnesium in the air–propane flame were established in the usual way. The air–propane flame was selected because of its steady combustion and because it gave adequate sensitivity and an extremely low radiative background so that it could be used with an unmodulated instrument relying on simple defocussing of resonance emission (Ca) in the flame. Commercial hollow-cathode lamps operating at 10 mA were used. Efficient aspiration and good nebulization were obtained with an air pressure of 20 lb/in^2; the flame used sufficiently little propane to be non-luminous when methyl isobutyl ketone was sprayed. A flame profile of the magnesium atoms showed their presence to be most marked low down, immediately over the cones of the combustion zone. The 2852 Å line[11] proved to be the most suitable for magnesium; the slit-width was 0·1 mm. The flame conditions for calcium were found to be more critical in that the absorbing atomic species were situated in a much more sharply defined band at the base of the outer mantle of the flame immediately above the primary reaction zone. The 4227 Å absorption line was found to be most suitable with a slit-width of

0·3 mm. Separate experiments proved that calcium and magnesium did not mutually interfere and that there was no interference from moderate concentrations of other ions such as nickel and chromium which are likely to be present in alumina. Some results obtained for the determination of known amounts of calcium and magnesium added to a saturated alum solution are given in Table I.

TABLE I.—DETERMINATION OF KNOWN AMOUNTS OF Ca, Mg, Fe AND Ni IN PRESENCE OF POTASSIUM ALUMINIUM SULPHATE (≡1 g OF Al_2O_3)

Magnesium		Calcium		Nickel		Iron	
Taken, μg	Found, μg	Taken, μg	Found, μg	Taken, μg	Found, μg	Taken, μg	Found, μg
3·04	3·10	20	19·75	11	11	7	7·5
5·5	5·8	50	49·50	22	22	21	18
6·08	6·05	50	46·5	36·7	34·5	35	33·5
6·08	6·10	50	49·5	55	56	56	60·5
6·08	6·10	50	46·5	55	56	84	82
6·08	5·6	50	49·5	55	58		
6·08	6·1	50	46·5	55	56		
6·08	6·7	50	48·0	73·4	74·5		
6·08	6·1	50	52·5				
8·5	8·6	70	70·05				
9·12	9·35	100	100·0				
12·16	12·05						

Because aluminium 8-hydroxyquinolate is extracted over the same pH range as the iron(III) and nickel complexes and is present in vastly greater amounts, co-precipitation with hydrated manganese(IV) oxide was used to separate and concentrate the iron and nickel. This technique has been used previously for the collection of iron(III) but there appears to be no record of its use for nickel.[12] A solution of the sample in sodium hydroxide was treated with 1–2 mg of manganese in the form of permanganate and sulphur dioxide was passed through the solution to reduce the permanganate to manganese(IV). This procedure proved to be very efficient for scavenging all traces of iron(III) and nickel from concentrated solutions of aluminium salts. No iron(III) or nickel could be detected in the filtrate by atomic-absorption measurements.

The hydrated manganese(IV) oxide may be filtered off immediately on paper pulp and is readily dissolved in a small amount of concentrated hydrochloric acid. Some hydroxylamine hydrochloride is added to ensure reduction of manganese(IV) to manganese(II), and the pH of the solution is then adjusted to 4·5 with acetate buffer for extraction of the nickel and iron(III) 8-hydroxyquinolates into methyl isobutyl ketone. Since the iron(III) and nickel contents of the potassium aluminium sulphate and the reagents used were unknown a blank experiment was performed simultaneously without the addition of trace amounts of iron(III) or nickel and this blank was deducted in drawing the calibration curves. An average blank for the potassium aluminium sulphate, obtained separately by deducting a blank for the reagents, corresponded to 0·0003% of iron and 0·00005% of nickel. Manganese(II) 8-hydroxyquinolate is not formed appreciably at pH 4·5 and therefore does not interfere with the extraction or the atomic-absorption measurements.

Some difficulties were encountered in measuring the atomic absorption due to iron in the air–propane flame at 2483 Å. The region of measurement in the flame

was not found to be critical, as it was with calcium, and the iron atoms appeared to be uniformly distributed throughout the flame above the primary reaction zone. The sensitivity of determination increased with decrease of slit-width down to a minimum of 0·2 mm and by increase of the current to the hollow-cathode lamp up to the maximum rating of 45 mA. With aqueous solutions, the calibration curves were linear over the range 10–50 ppm, but not at higher concentrations, see Fig. 2A(ii), which suggested lack of resolution of the 2483 Å line from neighbouring lines emitted by the hollow-cathode lamp. Because of lack of intensity it was not possible to close the slits to less than 0·2 mm. A similar state of affairs was found with extracts of iron(III) 8-hydroxyquinolate in methyl isobutyl ketone, Fig. 2B(ii).

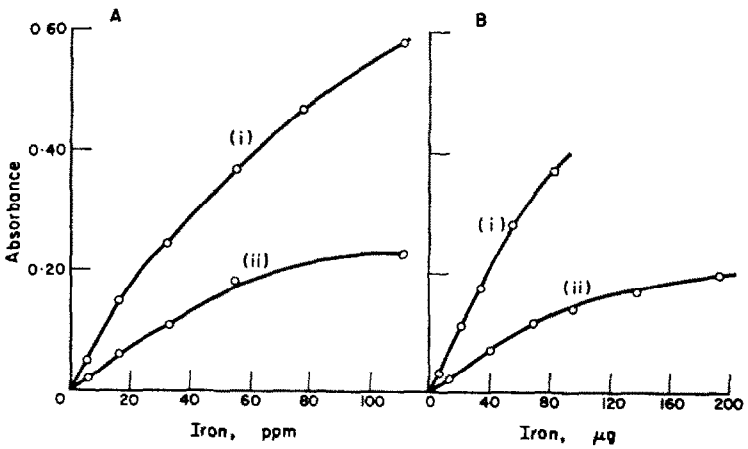

FIG. 2.—Comparison of microwave-excited source and hollow-cathode source in the determination of iron by atomic-absorption spectrophotometry.

(A) In aqueous solution
(*i*) microwave-source (*ii*) hollow-cathode
Optimized conditions for each.
(B) In methyl isobutyl ketone extract
(*i*) microwave-source (*ii*) hollow-cathode
Optimized conditions for each.

Accordingly, to obtain a much more intense source we constructed and used a microwave-excited discharge tube for iron by sealing some electrolytic iron powder and iodine in a quartz ampoule, thoroughly purged with argon and sealed off at *ca.* 1 mm Hg pressure of argon. The construction of such tubes has been described in a privious communication from this laboratory.[13] With this tube excited at 2450 Mc/s and operating at *ca.* 50 W, sufficient intensity was obtained to allow the slits to be closed to 0·05 mm, thus isolating the 2483 Å iron line from its neighbours much more effectively. Figures 2A(i) and 2B(i) show calibration curves obtained for aqueous and organic extracts of iron(III) with the microwave-excited source; it will be seen that the range of linearity is extended and the sensitivity increased considerably. This source was, therefore, used for all subsequent studies of the atomic-absorption of iron. Figure 3 shows the experimental arrangement of the atomic absorption apparatus and the microwave source and supply unit. A colour photograph of a microwave-excited thallium source has been published elsewhere by one of us.[14]

The stability of the iron discharge tube was not quite as good as that of a hollow-cathode lamp, but no special precautions were taken to stabilize it and it was found that provided frequent checks were made of the zero absorbance setting, no difficulty arose from this source. Our experience with other microwave tubes suggests that their output is as stable as that of a conventional hollow-cathode lamp. No special study was made of the best conditions for manufacture of an iron tube or of its effective life-time; it was entirely satisfactory over the period during which it was used.

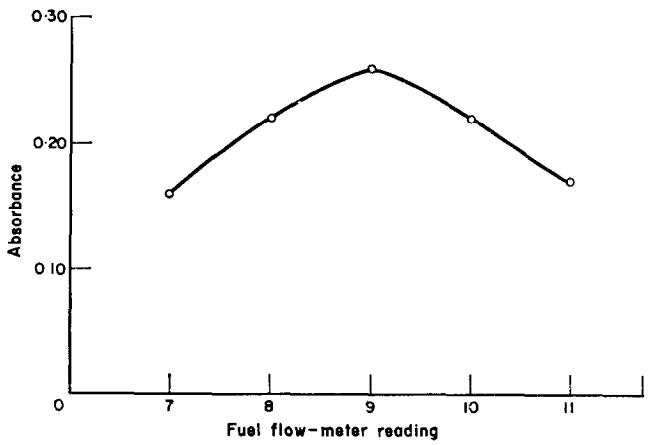

FIG. 4.—Variation of sensitivity with propane pressure for the determination of nickel at 3414 Å.

Aqueous solutions: air pressure 20 lb/in²: 59 ppm of Ni: slit-width 0·05 mm.

A conventional hollow-cathode lamp proved entirely satisfactory for the determination of nickel. The lines at 3414 and 2320 Å were examined for absorption measurements. With both lines the sensitivity increased with decrease of slit-width and reached a maximum at a particular propane pressure, see Fig. 4. The 2320 Å line was found to give a sensitivity about four times that of the 3414 Å line and yielded nearly linear calibration curves over the range 2–60 ppm with aqueous solutions. The same uniform distribution of nickel atoms was observed in the air–propane flame as was found for iron. Some results obtained for the determination of known amounts of iron and nickel added to a saturated solution of potassium alum are shown in Table I.

It is probable that the hydrated manganese(IV) oxide could also be used to co-precipitate calcium and magnesium, but iron hydroxide is more convenient because it can easily be separated from them by 8-hydroxyquinoline extraction whereas manganese can not; nor can manganese be masked against extraction along with the calcium and magnesium, even by potassium cyanide.

Further work is in progress on the evolution of similar procedures for chromium and cobalt in alumina. This communication does not describe the analysis of alumina itself, but demonstrates its feasibility. The amount of potassium aluminium sulphate solution used in these experiments corresponds to 1 g of alumina. The method is directly applicable to the analysis of soluble aluminium salts by the method of standard additions. Calibration curves are obtained by making standard additions of the metal

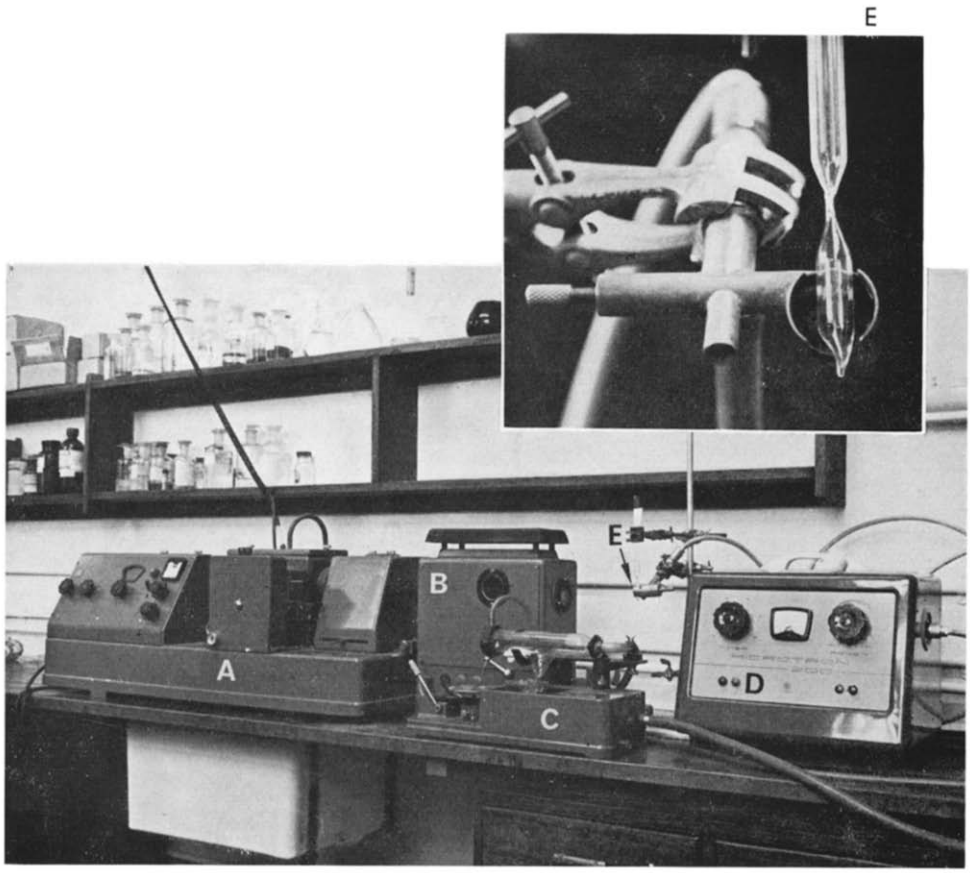

FIG. 3.—Apparatus for A.A.S. with microwave-excited source insert showing detail of microwave cavity and source-tube.
A—monochromator and read-out; B—flame-housing; C—nebulizer; D—microwave power supply; E—microwave cavity and discharge tube.

ion concerned to the aluminium salt solution and measuring against a *reagent* blank. These curves are then extrapolated, and the negative intercepts on the concentration axes represent the trace metal ion contents of the aluminium salt. In this way, the nickel content of the potassium aluminium sulphate used was found to be 5×10^{-5}%.

EXPERIMENTAL

Reagents

All reagents used were of analytical-reagent grade except where stated.

8-Hydroxyquinoline solutions, 2% and 6% in ethanol.

Iron(III) solution, 0·1%. Dissolve 8·687 g of iron(III) ammonium sulphate 12-hydrate in distilled water containing 10 ml of concentrated sulphuric acid and dilute to 1 l.

Buffer, pH 4·5. Dissolve 100 g of hydrated sodium acetate and 150 ml of glacial acetic acid in distilled water and dilute to 1 l.

Potassium aluminium sulphate solution. Dissolve 138·9 g of the 12-hydrate in distilled water and dilute to 1 l.

Standard calcium solution (5 *μg/ml*). Dilute 25 ml of 0·1*M* calcium chloride made by dissolving calcium carbonate in hydrochloric acid to 2 l. to give a stock 50 ppm solution. Dilute the stock solution tenfold just before use.

Standard magnesium solution (0·61 *μg/ml*). Dilute 25 ml of 0·1*M* magnesium sulphate (24·65 g of heptahydrate per l.) to 2 l. to give a 30·4-ppm stock solution. Just before use dilute 10 ml of stock solution to 500 ml.

Standard iron(III) solution (7 *μg/ml*). Dilute 10 ml of 0·1*M* iron(III) ammonium sulphate (48·521 g of the 12-hydrate per l.) to 1 l. with acidified distilled water stock solution. Just before use dilute 25 ml of the stock solution to 200 ml.

Standard nickel solution (3·67 *μg/ml*). Dilute 25 ml of 0·1*M* nickel sulphate (26·285 g of the hexahydrate per l.) solution to 1 l. to just before use dilute 25 ml of this solution to 1 l.

Apparatus

Hilger Uvispek (H 700) spectrophotometer with H 1100 atomic-absorption attachment. Premixed air–propane flame. Hilger aspirator-nebulizer (ca. 15% efficient for aqueous solutions). Perforated-plate burner head with *ca.* 10-cm flame. Hilger hollow-cathode lamps for calcium, magnesium and nickel.

Microwave signal generator (Microtron 200, Electromedical Supplies Ltd.) with 214 L cavity and coaxial cable.

Iron-iodine discharge tube constructed as detailed elsewhere.[13]

Methods

Calcium and magnesium

Transfer by pipette 70 ml of the potassium aluminium sulphate solution into each of a series of 400 ml beakers and add from 4 to 20 ml of standard calcium solution and from 2 to 15 ml of standard magnesium solution as required. Add 50 ml of 2*M* sodium hydroxide and 2 ml of the 0·1% iron(III) solution to each. Stir the suspensions of iron(III) hydroxide well and filter off each on a paper pulp pad. Wash the pads with water until alkali-free.

Transfer each funnel to the neck of a 250-ml separating funnel and dissolve the precipitates by slow addition of 2 ml of hydrochloric acid (1 + 1) to each. Wash the pads thoroughly with distilled water and dilute each solution to about 25 ml. To each funnel add 40 ml of saturated sodium chloride solution and 2 ml of 6% ethanolic 8-hydroxyquinoline solution. Then add 2*M* sodium hydroxide from a dropping tube till the first appearance of a black precipitate of iron(III) 8-hydroxyquinolate. Extract this complex at pH 4·5 by thorough shaking with 35 ml of ethyl acetate.

Discard the organic phase and add 2 ml of 6% ethanolic 8-hydroxyquinoline solution to each of the aqueous solutions; add enough sodium hydroxide solution to make the total 9 ml and give a pH $\geq$11·0 in each funnel. Extract the magnesium and calcium 8-hydroxyquinolate complexes by shaking vigorously for 1 min with 10 ml of methyl isobutyl ketone. Measure the atomic absorption of the calcium and magnesium by spraying the extracts into the air–propane flame, under the conditions described below, with methyl isobutyl ketone as a blank. Measure the absorption of a blank solution obtained by taking the reagents only through the procedure, and deduct it from the readings obtained. The calcium curve is linear over the range 10–100 *μg* and the magnesium curve from 1 to 10 *μg*. No effort was made to extend the curves beyond these limits.

If the same amount of potassium aluminium sulphate is added to the reagent blank solution a true calibration curve is obtained which passes through the origin. If the potassium aluminium sulphate

is excluded from the blank determination the negative intercept of the calibration curve on the concentration axis corresponds to the amount of calcium or magnesium in the potassium aluminium sulphate taken, *i.e.* the calcium and magnesium are determined by the method of standard additions.

Instrument settings

Calcium. Wavelength 4227 Å: slit-width 0·3 mm: lamp current 10 mA: burner height adjusted so that optical path is just above primary cones: air pressure 20 lb/in²: propane pressure sufficient to obtain a flame which is just non-luminous and has well defined primary cones when the organic extract is being sprayed.

Magnesium. Wavelength 285 Å: slit-width 0·1 mm: lamp current 10 mA: flame parameters as for calcium.

N.B. It is important to measure the absorption of the calcium first because of the tendency for calcium 8-hydroxyquinolate to precipitate in the extract.

Iron and nickel

Transfer by pipette 70 ml of the potassium aluminium sulphate solution into a series of 400-ml beakers and add from 1 to 10 ml of the standard iron solution and from 3 to 20 ml of the standard nickel solution. Add 50 ml of 4*M* sodium hydroxide to each and 3 ml or 0·01*M* potassium permanganate. Bubble sulphur dioxide through the solutions till all the permanganate has been converted into manganese dioxide, and filter off immediately on pulp pads. Wash the pads alkali-free with distilled water and transfer the funnels to the mouths of a series of 100-ml separating funnels. Dissolve the manganese dioxide on each pad with 4 ml of concentrated hydrochloric acid and wash the pads well with water. Dilute the solutions in each separatory funnel to 25 ml and ensure reduction to manganese(II) by adding a few crystals of hydroxylamine hydrochloride. Add 2 ml of 2% ethanolic 8-hydroxyquinoline solution and neutralize by addition of 4*M* sodium hydroxide till a *slight* turbidity appears. Then add 5 ml of the sodium acetate buffer, pH 4·5, and 10 ml of methyl isobutyl ketone. Shake thoroughly for 1 min to extract the 8-hydroxyquinolates of nickel and iron(III) and discard the aqueous layers. Spray the extracts into the air–propane flame and measure the atomic-absorbances for nickel and iron against methyl isobutyl ketone, using the instrumental settings described below. Measure the absorbance of a blank solution obtained by taking the reagents only through the procedure and deduct it from the readings. Both curves are linear from 10 to 80 μg.

The iron and nickel contents of the aluminium salt may be determined in the manner described for calcium and magnesium.

Instrument settings

Nickel. Wavelength 2320 Å: slit-width 0·1 mm: lamp current 35 mA: burner height sufficient to ensure that light path is above cones of primary zone: air pressure 20 lb/in²: propane pressure sufficient to obtain a non-luminous flame with well defined primary cones when the extracts are being sprayed.

Iron. Wavelength 2483 Å: slit-width 0·05 mm: flame conditions as for nickel.

Microwave cavity energized at 40–60 W with 2450 Mc/s radiation. Quartz tube containing Fe/I_2 slightly cooled by stream of air. Discharge initiated in tube by means of "Tesla" coil. The tube should be well run-in for 1 hr after manufacture and allowed to run for about 15 min each time before use.

Acknowledgement—We are grateful to the U.K.A.E.A. (Aldermaston) for a grant in aid of this work, and to the Science Research Council for the award of a special grant for the purchase of the atomic-absorption equipment. Our thanks are also due to the Central Electricity Generating Board (Midland Region) for granting study leave to one of us (G. B. M.) during the period in which this work was done.

Zusammenfassung—Die Bestimmung von Spuren Calcium und Magnesium in große Mengen Aluminium enthaltenden Lösungen erreicht man durch Mitfällung ihrer Hydroxide auf Eisen(III) hydroxid, Lösen des Niederschlags und Extraktion der 8-Hydroxychinolate von Calcium und Magnesium bei etwa pH 11 in Methylisobutylketon. Der Extrakt kann in die Luft-Propan-Flamme eines einfachen unmodulierten Spektrophotometers gesprüht werden; die Atomabsorptionsmessungen für Calcium und Magnesium werden bei 4227 bzw. 2852 Å gemacht. Die Nachweisgrenzen entsprechen 10 und 1 ppm Calcium bzw. Magnesium in Aluminiumoxid. Eisen und Nickel können auf Mangan(IV) oxidhydrat mitgefällt und ihre 8-Hydroxychinolate bei pH 4,5 extrahiert werden. Die Atomabsorptionsmessung dieser

Elemente bei 2483 und 2320 Å entspricht Nachweisgrenzen von 10 ppm in Aluminiumoxid. Für Calcium, Magnesium und Nickel lassen sich Hohlkathodenlampen verwenden; für Eisen gibt eine einfache mit Mikrowellen erregte Entladungsröhre viel, bessere Empfindlichkeit als eine Hohlkathodenlampe.

Résumé—On peut réaliser le dosage de traces de calcium et de magnésium dans des solutions à fortes concentrations en sels d'aluminium en coprécipitant leurs hydroxydes sur l'hydroxyde de fer(III), dissolvant le précipité et extrayant les 8-hydroxyquinoléinates de calcium et de magnésium en méthylisobutylcétone à pH voisin de 11. On peut pulvériser l'essai dans la flamme air-propane d'un spectrophotomètre simple non modulé et effectuer les mesures d'absorption atomique pour le calcium et le magnésium à 4227 et 2852 Å respectivement. Les limites de dosage correspondent à 10 et 1 p.p.m. de calcium et de magnésium dans l'alumine solide. On peut coprécipiter le fer et le nickel sur l'oxyde de manganèse(IV) hydraté et extraire leurs 8-hydroxyquinoléinates à pH 4,5. Les mesures d'absorption atomique pour ces éléments à 2483 et 2320 Å respectivement donnent des limites de détermination correspondant à 10 p.p.m. dans l'alumine. On peut utiliser des lampes à cathode creuse pour le calcium, le magnésium et le nickel, mais un tube à décharge excitée par microondes donne pour le fer une sensibilité bien meilleure qu'une lampe à cathode creuse.

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COMPUTER CALCULATION OF EQUILIBRIUM CONCENTRATIONS IN MIXTURES OF METAL IONS AND COMPLEXING SPECIES

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Summary—A method is described for calculating equilibrium concentrations of all species in multi-metal—multi-ligand mixtures from the pH of the solution, the total concentration of each metal and each complexing agent, and the relevant equilibrium constants (pK_a values and stability constants). No restriction is imposed on types of possible complexes, which can include mixed, hydrolysed, protonated and polynuclear species. Two examples are given. One of these comprises a 10-metal–10-ligand system (195 equilibrium constants). In the second system, mixed complex formation is important. The computer program is given.

KNOWLEDGE of equilibrium concentrations in solutions of metal ions and complex-forming species is important to the analyst in many ways. Thus, he may wish to establish the most favourable conditions for a determination, to assess the extent to which other species interfere, to develop new methods of analysis, or to compare the possible accuracies of existing procedures. The law of mass action provides the necessary basis for such calculations, given the relevant stability constants. However, when more than one type of metal ion and several different ligands are present at the same time, an iterative approach must be used. Such an approach, although possible by conventional means, is extremely laborious unless a digital computer is used.

Recently,[1] a computer program* was described for calculating the equilibrium concentrations of all species in a multi-metal–multi-ligand mixture, provided that the complexes formed were of the types ML, ML_2, ML_3, . . . ML_n. The only information needed was the pH of the solution, the total concentration of each metal and complexing agent, and the relevant equilibrium constants (pK_a values and stability constants). Such systems are also important as models for biological fluids. A comparable (but not general) procedure has been published for the computation of metal binding in the 2-metal–2-chelate system K^+, Mg^{2+}, ATP, EDTA.[2]

We have now developed an entirely general treatment for calculating concentrations in the presence of all types of metal complex equilibria, including the formation of mixed species (such as ML′L″ or M′LM″), hydrolysed species [such as M(OH), $M_2(OH)_3$ or M(OH)L], protonated species [such as LM(HL) or $M(HL)_2$], and polynuclear species [such as M_2L_3 or $M_2(OH)_2L_2$].

METHOD

If M^a, M^b, M^c, . . . represent the different kinds of metal ions, and L^r, L^s, L^t, . . . are different kinds of ligands, any complex that can be formed from them can be represented by $(M^a)_\alpha(M^b)_\beta(M^c)_\gamma \ldots (L^r)_\rho(L^s)_\sigma(L^t)_\tau \ldots (OH)_\omega$, where $\alpha, \beta, \gamma \ldots \rho, \sigma, \tau \ldots$ may be positive integers or zero, and ω may be a positive integer (for hydrolysed species), zero, or a negative integer (for protonated species). The concentration of

* The spelling *program* is used instead of *programme* out of deference to workers in the U.S. who first applied the term to computers.

any one of these complexes (including protonated ligand species and hydrolysed metal ions) is then given by

$$c_j = \beta_j[M^a]^\alpha[M^b]^\beta[M^c]^\gamma \ldots [L^r]^\rho[L^s]^\sigma[L^t]^\tau \ldots [OH]^\omega,$$

where β_j is the overall formation constant, so that the total concentration of metal i is:

$$[M^i]_T = [M^i] + \sum_{j=1}^{j=n} p_{ij}c_j \qquad (1)$$

where p_{ij} is the number of metal ions of M^i in the species j. A similar set of equations can be written for total ligand concentrations.

Using the program described in the Appendix, the computer reads in from cards the relevant set of values α, β, $\gamma \ldots \omega$, for each species, and the corresponding equilibrium constant. It then calculates free metal and ligand concentrations by the following iterative method.

Beginning with the crude approximation that complex formation is negligible (so that $[M^i] = [M^i]_T$, and $[L^x]$ can be calculated from $[L^x]_T$ by using the appropriate pK_a values), the machine computes the quantity on the right-hand side of equation (1) for each kind of metal ion, and similarly for each complexing species, to give quantities that can be designated as $[M^i]_T^{calc}$ and $[L^x]_T^{calc}$, respectively. The initial estimates of $[M^i]$ and $[L^x]$ are then replaced by $[M^i]([M^i]_T/[M^i]_T^{calc})^{1/2}$ and $[L^x]([L^x]_T/[L^x]_T^{calc})^{1/2}$. With these new estimates the calculations are repeated, to obtain better values of $[M^i]$ and $[L^x]$. The process is continued until all values of $[M^i]_T^{calc}$ and of $[L^x]_T^{calc}$ differ from the corresponding values of $[M^i]_T$ and of $[L^x]_T$ by less than a specified quantity. (For the results given in Tables I and II this was chosen to be 0·001 % of $[M^i]_T$ and of $[L^x]_T$.) Within this accuracy, the final values of $[M^i]$ and $[L^x]$ satisfy all equations for metal and ligand concentrations. They are then used to compute the equilibrium concentrations of all species, and the results are finally printed out in tabular form.

DISCUSSION

The program has been tested for a system containing ten different kinds of metal ions and ten substituted iminodiacetic acids of the types R—$N(CH_2COO^-)_2$, and having a total of 195 species for which equilibrium constants are available.[3] These include pK_a values for the ligands and for hydrolysed metal ions, and constants for protonated and hydrolysed complexes. An IBM 360/50 electronic computer took 7·0 min to calculate all of the equilibrium concentrations at pH 10 for a solution in which the total concentration of each complexing species was 0·002M and the total concentration of each metal ion was 0·001M. These results are given in Table I.

They are of some interest in providing a quantitative measure of the relative metal-binding abilities of these ligands under the particular experimental conditions chosen, and also in demonstrating preferences among the different metal ions for individual ligands. Thus, magnesium, calcium and manganese form mainly their 1:1 complexes with the ligand where R is $^-OOC—CH_2—$, whereas the most stable 1:1 complexes of cobalt, nickel, copper and zinc are with the ligand where R is $NH_2—CH_2—CH_2—$. On the other hand, complex formation is only slight when R is $NC—CH_2—$ or $(CH_3)_3\overset{+}{N}—CH_2—CH_2—$. Strontium and barium show little discrimination between the four ligands for which R is $HO—CH_2—CH_2—$, $(CH_3)_3C—CH_2—CH_2—$, $^-OOC—CH_2—$ and $NH_2—CO—CH_2—$.

As a further test of the program, it has been applied to the published data[4] for mixed complex formation by nickel and zinc with pyruvate and glyoxalate ions and

TABLE I.—DISTRIBUTION OF METALS IONS AMONG SUBSTITUTED IMINODIACETIC ACIDS

Species	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10
L	126	324	223	1922	269	2	17	1272	1879	796
HL	56	17	20	—	22	21	9	1	—	30
H_2L	—	—	—	—	—	—	—	—	—	—
H_3L	×	×	×	×	×	×	×	×	×	×
MgL	42	108	55	6	34	8	517	46	17	46
CaL	9	173	95	2	7	1	533	145	13	10
SrL	11	237	192	4	17	1	197	170	33	14
BaL	9	164	156	8	22	1	211	186	35	15
MnL	21	76	50	1	22	62	300	71	4	21
MnL_2	38	141	136	×	24	1	×	18	1	15
CoL	1	5	4	—	17	214	77	2	—	1
Co(HL)	×	×	×	×	×	—	×	×	×	×
CoL_2	252	25	77	22	105	5	×	5	6	174
Co(OH)L	×	8	×	×	×	×	×	×	×	×
NiL	—	1	1	—	4	149	9	—	—	—
Ni(HL)	×	×	×	×	×	—	×	×	×	×
NiL_2	216	28	53	2	110	222	×	2	1	201
Ni(OH)L	×	—	×	×	×	×	×	×	×	×
CuL	—	2	3	—	8	101	1	—	—	—
CuL_2	92	5	13	1	26	×	×	—	—	33
Cu(OH)L	1	39	29	×	80	544	×	×	×	×
$Cu(OH)_2L$	×	×	21	×	×	×	×	×	×	×
ZnL	1	9	8	—	6	195	97	3	—	1
ZnL_2	246	14	44	3	55	×	×	1	1	98
Zn(OH)L	×	32	17	×	13	145	×	×	×	×
$Zn(OH)_2L$	×	4	×	×	×	×	×	×	×	×
$Zn(OH)L_2$	×	×	8	×	×	×	×	×	×	×
CdL	—	3	2	—	6	21	34	5	—	—
CdL_2	16	186	231	—	416	40	×	24	—	12

At pH 10. All concentrations in μM. The total concentrations of each metal ion and complexing species were 1000 μM and 2000 μM, respectively.

Concentrations of free metal ions (rounded off to 1 μM); Mg, 121; Ca, 12; Sr, 5; Ba, 193, Mn, 1; Co, 0; Ni, 0; Cu, 0; Zn, 0; Cd, 4. An × indicates that no stability constant was available for a particular species, or that the species was not known, whereas a dash implies that the concentration was less than 0·5 μM. Constants were also included for $MnOH^+$, $CoOH^+$, $NiOH^+$, $Cu_2(OH)_2^{2+}$, $Cu_3(OH)_4^{2+}$, $ZnOH^+$ and $CdOH^+$. The ligands were all of the type $R—N(CH_2COO^-)_2$, where R is $CH_3—$, $HO—CH_2—CH_2—$, $(CH_3)_3C—CH_2—CH_2—$, $(CH_3)_3\overset{+}{N}—CH_2—CH_2—$, $CH_3S—CH_2—CH_2—$, $NH_2—CH_2—CH_2—$, $^-OOC—CH_2—$, $NH_2—CO—CH_2—$, $NC—CH_2—$, and $C_2H_5O—CO—NH—CH_2—CH_2—$, for ligands 1–10 respectively.

glycine. Equilibrium concentrations of 28 different species were calculated in 16 sec for a solution at pH 9 and 0·001M in each metal ion and complexing species. These results are summarized in Table II, rounded off to 1 μM.

An alternative program has also been developed to solve simultaneously the $(m + n)$ non-linear equations that can be written to express total concentrations in systems containing m kinds of metal ions and n kinds of complexing species. The method chosen makes use of a Newton–Raphson procedure,[5] which we have generalized to deal iteratively with $(m + n)$ unknowns. This technique had already proved useful for the simultaneous solution of two equations in the refinement program GAUSS[6] (which was developed from a similar program written by Tobias[7]) for dealing with equilibria in systems of one metal and one ligand. When the method was employed with the 10-metal–10-ligand system, convergence was not satisfactory, possibly because the available precision of the computer was insufficient for the calculations. However, for systems containing only small numbers of metals and ligands (up to about three

TABLE II.—MIXED COMPLEX FORMATION BY NICKEL AND ZINC IONS

Species	Glycine	Pyruvate	Glyoxalate
L	2·48	818	879
HL	12	—	—
H_2L	—	×	×
NiL	382	4	3
NiL_2	67	—	×
NiL_3	—	×	×
ZnL	143	11	3
ZnL_2	5	—	×
ZnL_3	—	×	×
Ni(gly)(pyruv)	81	Zn(gly)(pyruv)	62
$Ni(gly)_2(pyruv)$	15	$Zn(gly)_2(pyruv)$	3
$Ni(gly)_2(pyruv)_2$	3	$Zn(gly)_2(pyruv)_2$	1
Ni(gly)(glyox)	90	Zn(gly)(glyox)	9
$Ni(gly)_2(glyox)$	15	$Zn(gly)_2(glyox)$	—
$Ni(gly)_2(glyox)_2$	1	$Zn(gly)_2(glyox)_2$	—

At pH 9. All concentrations in μM. Total concentrations of each metal ion and complexing species, 1000 μM. Free nickel ion, 341 μM; free zinc ion, 764 μM.

of each) calculations were appreciably faster than by the other program.

The two types of program are thus complementary. The simpler program deals reliably with the more complicated systems, while the Newton–Raphson approach calculates more rapidly the relevant concentrations in simpler systems.

A continuing handicap to the application of either of these programs to equilibria in metal–ligand mixtures is the small number of recorded stability constants for mixed complexes and also for protonated and hydrolysed species. Existing computer programs such as GAUSS[6] and LETAGROP[8] can be used to calculate stability constants for polynuclear, protonated or hydrolysed complexes but hitherto no general program has been available for similar computations for mixed species, notwithstanding their great importance for a quantitative understanding of metallo–enzyme–substrate interactions. For this reason we have also developed a general program for calculating the stability constant of any type of mixed complex from titration data, provided the constants for the other complexes are known. This program uses the Newton–Raphson method. Thus, in principle, it should now be possible to obtain constants for all of the types of complexes that need to be considered in multi-metal–multi-ligand systems.

These programs have further applications, particularly in the quantitative investigation of metal ion equilibria in biological systems, in metal ion toxicity studies, and in dealing with simultaneous buffering with respect to more than one metal ion.

Zusammenfassung—Eine Methode zur Berechnung der Gleichgewichtskonzentrationen aller Spezies in Mischungen mehrerer Metalle und mehrerer Liganden aus dem pH der Lösung, den Gesamtkonzentrationen jedes Metalls und jedes Komplexbildners und den einschlägigen Gleichgewichtskonstanten (pK_a-Werten und Stabilitätskonstanten) wird beschrieben. Die Typen möglicher Komplexe unterliegen keiner Beschränkung: es können gemischte, hydrolysierte, protonierte und mehrkernige Spezies vorkommen. Zwei Beispiele werden angegeben. Eines davon enthält ein System aus 10 Metallen und 10 Liganden (195 Gleichgewichtskonstanten). Im zweiten System ist die Bildung gemischter Komplexe von Bedeutung. Das Rechenprogramm wird angegeben.

Résumé—On décrit une méthode pour calculer les concentrations d'équilibre de toutes les espèces dans des mélanges multi-métaux-multi-ligands à partir du pH de la solution, de la concentration totale de chaque métal et de chaque agent de complexation et des constantes d'équilibre correspondantes (valeurs de pK_a et constantes de stabilité). Aucune restriction n'est imposée quant aux types des complexes possibles, qui peuvent inclure des espèces mixtes, hydrolysées, protonées ou polynucléaires. On donne deux exemples. L'un d'eux comprend un système 10-métaux-10-ligands (195 constantes d'équilibre). Dans le second système, la formation de complexe mixte est importante. On donne le programme de computation.

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APPENDIX

The computer program described above is in two parts. The main program, which we have called COMICS (*c*oncentrations *of* *m*etal *i*ons and *c*omplexing *s*pecies), is used to read the data, to set up initial approximations for the free metal and free ligand concentrations, and later to print out the results. The iterative procedure for adjusting the free metal and free ligand concentrations is carried out in a subroutine called COGS (*c*oncentrations *of* *g*eneralised *s*pecies), which returns the computed concentrations of free metal ions, free ligands, and of all complex species to the main program for tabulation, after a satisfactory degree of convergence has been achieved.

The program, as listed below, is intended to calculate concentrations at a series of pH values. In order to speed the calculation for the second and subsequent pH values, the initial approximations for the concentrations of free metals and free ligands for the nth point are taken to be the final values of these quantities for the $(n-1)$th point. The listing of the program includes a description of the input data, and is followed by a list of the variables used, and by a simplified flow sheet showing the calculation method.

Computer program COMICS

```
C       PROGRAM COMICS
C
C       INPUT DATA
C     1 NUMBER OF SETS OF EXPERIMENTAL CONDITIONS TO BE RUN
C       (I2)
C     2 TITLE OF FIRST (SECOND, THIRD ETC.) EXPERIMENT ANY
C       CHARACTERS IN COLS. 1-80.
C     3 NUMBER OF LIGANDS, OF METALS, AND OF COMPLEX SPECIES
C       FORMED (INCLUDING PROTONATED FORMS OF LIGAND,
C       AND HYDROLYSED METAL IONS), (2I2,I3)
C     4 A CARD FOR EACH COMPLEX SPECIES LISTING THE NUMBER OF
C       MOLECULES OF LIGAND (1), (2), (3) ETC. UP TO (10) THE NUMBER
C       OF IONS OF METAL (1), (2) (3) ETC. UP TO (10)  THE
C       NUMBER OF HYDROXYL IONS (A POSITIVE INTEGER), OR OF
C       PROTONS (A NEGATIVE INTEGER) THE LOGARITHM OF THE
C       CUMULATIVE ASSOCIATION CONSTANT OF THE SPECIES,
C       (21I2,8X,F8·4)
C     5 THE TOTAL CONCENTRATION OF EACH LIGAND (10F8·4)
C     6 THE TOTAL CONCENTRATION OF EACH METAL (10F8·4)
C     7 A SERIES OF CARDS BEARING PH AND INDEX INDEX = 0 FOR
C       ALL BUT LAST CARD OF EXPERIMENT WHEN INDEX = 1
C       (F10·4,I1)
```

```
      C     8  THEN RETURN TO ITEM 2 UNTIL TOTAL NUMBER OF EXPERI-
      C          MENTS (GIVEN BY ITEM 1) HAS BEEN REACHED.
      C
S.0001          DIMENSION C(200), Y1(10), Y2(10), Y3(10), Y4(10), BTOT(10),
     1 CLTOT(10), ITX(10), VX(10), ML(10,200), MM(10,200), MN(200),
     2 AL(10,200), 2AM(10,200), AN(200), B(200), E(200), DM(10), DMY(10),
     3 TITLE(20)
      C
S.0002          COMMON C,Y1,Y2,Y3,Y4,BTOT,CLTOT,TX,VX,1ML,MM,MN,AL,
     1 AM,AN,NL,NM,N,B,UX,IPT
      C
S.0003        1 FORMAT (I2)
S.0004        2 FORMAT (21I2,8X,F8·4)
S.0005        6 FORMAT (1X, I3, 2X,21(2X,I2),3X,F8·4)
S.0006        8 FORMAT (10F8·4)
S.0007        9 FORMAT (24H TOTAL CONCN. OF METAL (,I2,4H) = ,E10·3)
S.0008       10 FORMAT (25H TOTAL CONCN. OF LIGAND (,I2,4H) = ,E10·3)
S.0009       11 FORMAT(13X,2HC1,9X,2HC2,9X,2HC3,9X,2HC4,9X,2HC5,9X,2HC6,9X
     1 2HC7,9X 1,2HC8, 9X,2HC9,8X,3HC10)
S.0010       12 FORMAT (2I2,I3)
S.0011       17 FORMAT (F10·4,I1)
S.0012       30 FORMAT (///' PH = ',F6·3)
S.0013       33 FORMAT (8X,93HL1 M L2 L3 L4 L5 L6 L7 L8 L9 L10 M1
     1 M2 M3 1M4 M5 M6 M7 M8 M9 M10 OH LOG.BETA /)
S.0014       34 FORMAT ('FREE METALS')
S.0015       35 FORMAT (8X,10(1X,1PE10·3))
S.0016       36 FORMAT ('FREE LIGANDS')
S.0017       37 FORMAT ('COMPLEX SPECIES')
S.0018       43 FORMAT (1X,I3,1H-,I3,10(1X,1PE10·3))
S.0019      130 FORMAT (20A4)
S.0020      131 FORMAT (1X,20A4//)
S.0021      999 FORMAT (1H1)
      C
S.0022          WRITE (3,999)
S.0023          READ (1,1) NJ
S.0024          NJD=0
S.0025      106 READ (1,130) (TITLE(I),I=1,20)
S.0026          WRITE (3,131) (TITLE(I),I=1,20)
S.0027          WRITE (3,33)
S.0028          READ (1,12) NL,NM,N
S.0029          DO 7 J=1,N
S.0030        3 READ (1,2) (ML(I,J),I=1,10),(MM(I,J),I=1,10),MN(J),E(J)
S.0031        7 WRITE (3,6) J,(ML(I,J),I=1,10),(MM(I,J),I=1,10),MN(J),E(J)
S.0032          READ (1,8) (CLTOT(I),I=1,10)
S.0033          READ (1,8) (BTOT(I),I=1,10)
S.0034          WRITE (3,10) (I,CLTOT(I),I=1,NL)
S.0035          WRITE (3,9) (I,BTOT(I),I=1,NM)
S.0036          HX=ALOG(10·0)
S.0037          IPT=1
S.0038          DO 4 J=1,N
S.0039          AN(J)=MN(J)
S.0040          DO 4 I=1,10
S.0041          AL (I,J)=ML(I,J)
S.0042        4 AM(I,J)=MM(I,J)
S.0043          DO 13 I=1,N
S.0044       13 B(I)=EXP(HX*E(I))
S.0045          DO 14 I=1,NM
S.0046       14 Y1(I)=BTOT(I)*0·00001
S.0047          DO 15 I=1,NL
S.0048       15 Y3(I)=CLTOT(I)*0·00001
S.0049       16 READ (1,17) PH,INDEX
S.0050          WRITE (3,30) PH
S.0051          UX=EXP(HX*PH)
S.0052          IF (IPT-1) 18,18,27
```

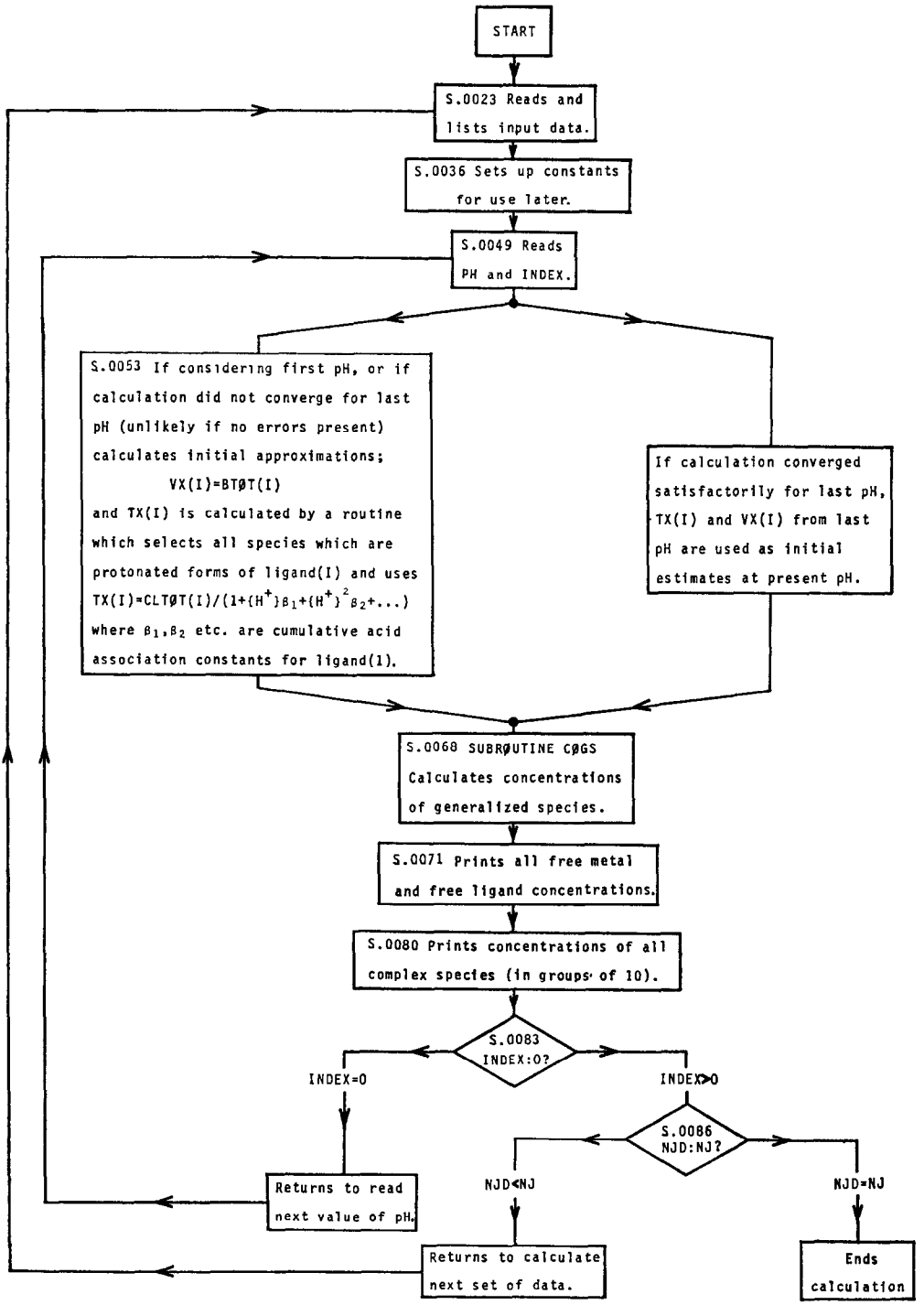

FIG. 1.—Flow sheet for computer program COMICS.

(*Continued*)

```
S.0053      18  DO 19 I=1,NM
S.0054      19  VX(I)=BTOT(I)
S.0055          DO 20 I=1,NL
S.0056          DMY(I)=1·0
S.0057          DO 22 J=1,N
S.0058          IF (ML(I,J)) 22,22,200
S.0059     200  DO 21 K=1,NM
S.0060          IF (MM(K,J)) 22,21,22
S.0061      21  CONTINUE
S.0062          DM(I)=(EXP(HX*E(J)))*UX**MN(J)
S.0063          DMY(I)=DMY(I)+DM(I)
S.0064      22  CONTINUE
S.0065      20  CONTINUE
S.0066          DO 23 I=1,NL
S.0067      23  TX(I)=CLTOT(I)/DMY(I)
      C
S.0068      27  CALL COGS
      C
S.0069          WRITE (3,11)
S.0070          WRITE (3,34)
S.0071          WRITE (3,35) (VX(I),I=1,NM)
S.0072          WRITE (3,36)
S.0073          WRITE (3,35) (TX(I),I=1,NL
S.0074          WRITE (3,37)
S.0075          KP=0
S.0076      40  KP=KP+1
S.0077          KN=10*KP
S.0078          KM=KN−9
S.0079          IF (KN−N) 41,42,42
S.0080      41  WRITE (3,43) KM,KN,(C(I),I=KM,KN)
S.0081          GO TO 40
S.0082      42  WRITE (3,43) KM,N(C(I),I=KM,N)
S.0083          IF (INDEX) 31,16,31
S.0084      31  NJD=NJD+1
S.0085          WRITE (3,999)
S.0086          IF (NJD−NJ) 106,32,32
S.0087      32  STOP
S.0088          END
S.0001          SUBROUTINE COGS
      C
S.0002          DIMENSION TERM(200), TERN(200),C(200),Y1(10),Y2(10),Y3(10),
               1 Y4(10),1BTOT(10),CLTOT(10),TX(10),VX(10),ALO(10),BO(10),TY(10),
               2 VY(10),2ML(10,200),MM(10,200),MN(200)AL(10,200),AM(10,200),
               3 AN(200),B(200)
      C
S.0003          COMMON C,Y1,Y2,Y3,Y4,BTOT,CLTOT,TX,VX,1ML,MM,MN,AL,
               1 AM,AN,NL,NM,N,B,UX,IPT
      C
S.0004      99  FORMAT ('NUMBER OF ITERATIONS = ',I4)
S.0005     998  FORMAT ('ITERATION DID NOT CONVERGE')
      C
S.0006          NIT=0
S.0007          DO 1 K=1,N
S.0008       1  TERM(K)=B(K)*UX**MN(K)
S.0009       2  DO 3 K=1,N
S.0010       3  TERN(K)=TERM(K)
S.0011          DO 4 K=1,N
S.0012          DO 4 J=1,NM
S.0013       4  TERN(K)=TERN(K)*VX(J)**MM(J,K)
S.0014          DO 5 K=1,N
S.0015          DO 15 J=1,NL
```

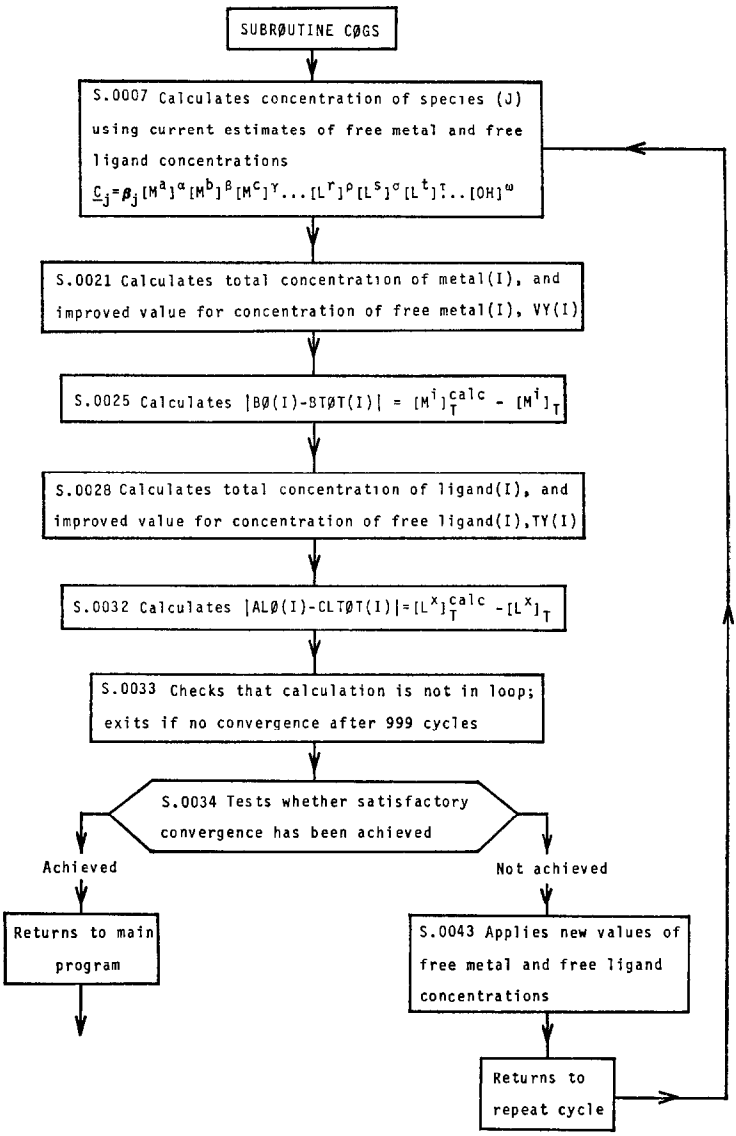

FIG. 2.—Flow sheet for sub-routine COGS.

List of variables used in program COMICS

NJ	Number of separate jobs to be run with program.
NJD	Number of jobs done.
TITLE(I)	Array used to print headings.
NL	Number of ligands in system under study.
NM	Number of metals in system under study.
N	Number of complex species in system under study (including protonated forms of ligand, and hydrolysed metal species).
ML(I,J), AL(I,J)	Number of molecules of ligand(I) in species(J), in fixed and floating point.
NM(I,J), AM(I,J)	Number of atoms of metal(I) in species(J), in fixed and floating point.
MN(J), AN(J)	Number of protons in species(J), in fixed and floating point.
E(J)	Log of cumulative association constant for species(J).
CLTOT(I)	Total concentration of ligand(I).

```
S.0016      15  TERN(K)=TERN(K)*TX(J)**ML(J,K)
S.0017       5  C(K)=TERN(K)
S.0018         NIT=NIT+1
S.0019         DO 7 I=1,NM
S.0020         BO(I)=VX(I)
S.0021         DO 8 K=1,N
S.0022       8 BO(I)=BO(I)+AM(I,K)*C(K)
S.0023         RATIO=BO(I)/BTOT(I)
S.0024         VY(I)=VX(I)/SQRT(RATIO)
S.0025       7 Y2(I)= ABS(BO(I)—BTOT(I))
S.0026         DO 9 I=1,NL
S.0027         ALO(I)=TX(I)
S.0028         DO 10 K=1,N
S.0029      10 ALO(I)=ALO(I)+AL(I,K)*C(K)
S.0030         RATIO=ALO(I)/CLTOT(I)
S.0031         TY(I)=TX(I)/SQRT(RATIO)
S.0032       9 Y4(I)= ABS(ALO(I)−CLTOT(I))
S.0033         IF (NIT−999) 11,11,999
S.0034      11 DO 12 I=1,NM
S.0035         IF (Y1(I)−Y2(I)) 14,12,12
S.0036      12 CONTINUE
S.0037         DO 13 I=1,NL
S.0038         IF (Y3(I)−Y4(I)) 14,13,13
S.0039      13 CONTINUE
S.0040         IPT=IPT+1
S.0041         WRITE (3,99) NIT
S.0042         RETURN
S.0043      14 DO 16 I=1,NL
S.0044      16 TX(I)=TY(I)
S.0045         DO 17 I=1,NM
S.0046      17 VX(I)=VY(I)
S.0047         GO TO 2
S.0048     999 WRITE (3,998)
S.0049         IPT=1
S.0050         RETURN
S.0051         END
```

BTOT(I)	Total concentration of metal(I).
HX	$\log_e 10{\cdot}0$.
B(I)	Exponential form of constant E(I).
IPT	Indicator used in obtaining initial approximations for free metal and free ligand concentrations. IPT = 1 for first point (or if last point was non-convergent). IPT > 1 otherwise.
Y1(I)	Convergence parameter for total metal(I).
Y2(I)	(Calculated − experimental) concentration of total metal(I).
Y3(I)	Convergence parameter for total ligand(I).
Y4(I)	(Calculated − experimental) concentration of total ligand(I). Convergence is assumed to be satisfactory when Y2(I) < Y1(I) and Y4(I) < Y3(I) for all values of I.
PH	pH
INDEX	Index = 0 for all cards bearing pH values, up to last card when index = 1.
UX	Exponential form of pH.
VX(I)	Current estimate of concentration of free metal(I).
TX(I)	Current estimate of concentration of free ligand(I).
DM(I), DMY(I)	Dummy variables used in calculation of initial estimate of TX(I).
KM, KN, KP	Integers used in tabulation routine.
C(I)	Concentration of complex species(I).
TERM(K), TERN(K)	Dummy variables used for calculation of species concentrations C(J).
BO(I)	Variable used in summation of calculated total metal(I).
ALO(I)	Variable used in summation of calculated total ligand(I).
RATIO	Calculated total metal(I)/experimental total metal(I), or calculated total ligand(I)/experimental total ligand(I).
VY(I)	Variable used to store improved value of VX(I).
TY(I)	Variable used to store improved value of TX(I).

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END-POINT SHARPNESS IN THERMOMETRIC TITRIMETRY

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Summary—It is shown that the sharpness of an end-point in a thermometric titration where the simple reaction

$$A + B \rightleftharpoons AB$$

takes place, depends on Kc_A' where K is the equilibrium constant for the reaction, and c_A' is the total concentration of the titrand (A) in the reaction mixture. The end-point is sharp if, (*i*) the enthalpy change in the reaction is not negligible, and (*ii*) $Kc_A' > 10^3$. This shows that it should, for example, be possible to titrate 0·1*M* acid, $pK_A = 10$, using a thermometric end-point. Some aspects of thermometric titrimetry when $Kc_A' < 10^3$ are also considered.

IN A thermometric titration the rate of change of temperature of a reaction vessel, dT/dt, is measured as a titrant is added at a constant rate. A sudden change in dT/dt marks the end-point, and it is the sharpness of this change that determines the analytical usefulness of the technique. The shape of the experimental curve of temperature *vs.* titrant volume added (the "thermogram") depends upon:

(*i*) the heat capacity of the system, and its change during the titration,
(*ii*) the rate of heat exchange of the system with its surroundings,
(*iii*) the molar enthalpy change in the reaction, and any enthalpy of dilution,
(*iv*) the amount of product formed for a given addition of titrant.

The design of the titration assembly determines (*i*) and (*ii*), and it is always possible in principle to convert the "thermogram" into an "enthalpogram" representing the relationship between the heat evolved or absorbed in the reaction and the amount of titrant added. If the molar enthalpy change in the reaction is small, the change in slope of both the thermogram and of the derived enthalpogram at the end-point will necessarily be small, and the reaction is unsuitable for thermometric titrimetry. The change will be large, and the end-point sharp, when the molar enthalpy change is large and the reaction is complete. If, however, the reaction is not complete near the end-point, the slope of the enthalpogram will change more slowly in this region, and the end-point will be correspondingly less distinct however large the enthalpy change may be. It is known from experiment that it is possible to use the thermometric method for end-point detection in cases where the reaction is insufficiently complete for other methods to be used. For example, acids as weak as boric acid, or the ammonium ion, can be titrated successfully in this way.[1] For even weaker acids, where the end-point is not detectable with sufficient sharpness for analytical purposes, enthalpograms can be utilized to calculate the thermodynamic parameters of the proton equilibria

involved.[2] Several authors have discussed methods of doing this[2,3,4] for these and other reactions but there appears to be no published treatment which can lead at once to an appreciation of the likelihood of a given reaction yielding a thermometric end-point of sufficient sharpness for practical use. It is the purpose of this paper to remedy this lack for a simple class of reactions of considerable analytical importance.

Consider the normal type of titration procedure where a small volume of a concentrated solution of a reagent B is added, either in successive aliquots, or continuously, to a dilute solution of a reagent A, an equilibrium of the following type being established:

$$A + B \rightleftharpoons AB.$$

The concentrations of A, which is initially in excess, and of B, are c_A and c_B respectively. Only a small volume of the titrant solution B is added, but, even so, the total concentration of the species A in the reaction vessel will change slightly from its initial value to some other value c_A', after a volume V_B of titrant has been added to the original volume, V_A, of titrand. Assume that a proportion α of B is converted into AB when the total concentration of B in the reaction vessel is c_B', and define a coefficient β such that

$$\beta = c_B'/c_A' = c_B V_B/c_A V_A. \tag{1}$$

The free concentrations of the species are therefore

$$\begin{aligned} [A] &= c_A' - \alpha c_B' = c_A'(1 - \alpha\beta) \\ [B] &= c_B'(1 - \alpha) \\ [AB] &= \alpha c_B'. \end{aligned} \tag{2}$$

If concentrations are assumed to be equal to activities, the formation constant, K, for the species AB, can be written

$$K = \frac{[AB]}{[A][B]} = \frac{\alpha}{c_A'(1 - \alpha\beta)(1 - \alpha)}. \tag{3}$$

This is a quadratic equation in α which can be transformed into:

$$\alpha^2\beta - \alpha(\beta + \zeta + 1) + 1 = 0 \tag{4}$$

where $\zeta = 1/Kc_A'$. The quantity ζ is almost, though not quite, constant during the titration since V_A is always much larger than V_B in any normal type of thermometric titration and $c_A \sim c_A'$.

Equation (4) has two roots, only one of which is physically significant, namely,

$$\alpha = \frac{(\beta + \zeta + 1) - [(\beta + \zeta + 1)^2 - 4\beta]^{1/2}}{2\beta}. \tag{5}$$

The proportion α of added B that has been converted into AB is therefore a function of β, the ratio of total B to total A in the reaction vessel, and of ζ, and can be calculated for chosen values of these variables.

For simplicity, it is assumed that the experimental thermogram has been converted into an enthalpogram, and that all heat of dilution effects have been allowed for ("corrected enthalpogram"). If the molar enthalpy change in the formation of AB is ΔH_R, then the total heat, q_R, (after correction for heat of dilution effects) evolved in

the titration up to the point at which a volume V_B of the titrant has been added, is given by

$$\begin{aligned} q_R &= -[AB](V_A + V_B)\Delta H_R \\ &= -c_B V_B \alpha \Delta H_R \end{aligned} \tag{6}$$

from (2) and the definition of α. The corrected enthalpogram is a plot of q_R against volume V_B of titrant added and will be linear as long as α remains constant. If every molecule of B added reacts to form AB, then $\alpha = 1$ as long as A is in excess, *i.e.*, while $\beta < 1$. At, and after, the equivalence point ($\beta = 1$)

$$\alpha = \frac{c_A V_A}{c_B V_B}, \tag{7}$$

which with equation (6) gives

$$q_R = -c_A V_A \Delta H_R \qquad (\beta \geqslant 1) \tag{8}$$

i.e., after the equivalence point q_R is independent of V_B. The change in slope of the corrected enthalpogram at the end-point is sharp if ΔH_R is large enough, and the reaction then has an easily detectable thermometric end-point. When the reaction is incomplete, α deviates from unity before the equivalence point is reached, and the limiting form of the enthalpogram as given by equation (8) is not even approximately attained until an excess of B has been added.

Equation (5) shows that at a given value of β, α depends on ζ. The simplest case is at the equivalence point where equation (3) takes the form

$$1/\zeta = Kc_A' = \alpha/(1 - \alpha)^2.$$

For α to be 0·99 at this point, Kc_A' must be about 10^4. This value of α would correspond to a very sharp thermometric end-point. A more detailed picture of the effect of the formation constant on the sharpness of the end-point can be obtained as follows. From equations (1) and (6)

$$\frac{-q_R}{c_A V_A \Delta H_R} \equiv \xi = \alpha\beta \tag{9}$$

where ξ is a dimensionless variable, the "reduced heat output", and can be calculated for arbitrary values of β and ζ, from equations (5) and (9). When ξ is plotted against β, a set of "reduced enthalpograms", each characteristic of a particular value of ζ, is obtained. These differ from experimental corrected enthalpograms only in scale, and give an immediate impression of the expected end-point sharpness corresponding to any value of ζ, provided only that ΔH_R is large enough for the change in temperature of the system due to the heat of the reaction to be measurable experimentally. A set of such curves is shown in Fig. 1. From this it appears that a reasonably sharp end-point can be expected for a reaction with $\zeta \leqslant 10^{-3}$, *i.e.*, $Kc_A' \geqslant 10^3$. For larger values of ζ the curvature of the reduced enthalpogram near the end-point shows that a sharp thermometric end-point would not be obtained under any experimental conditions. The conditions under which a weak monobasic acid can be titrated thermometrically with a strong base follow immediately. The titrand (A) is the weak acid HX and the

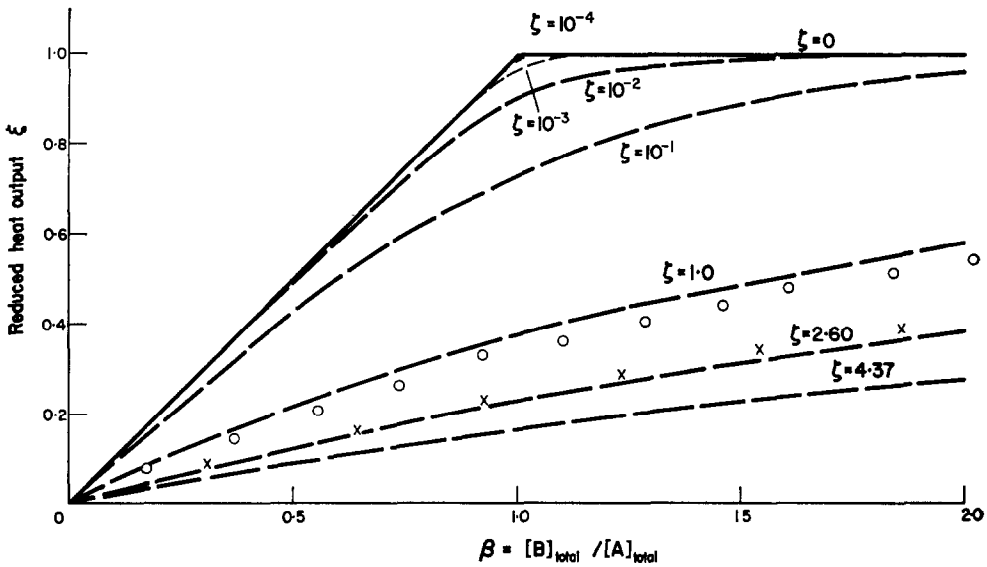

FIG. 1.—Reduced enthalpograms for varying values of ζ.
The full line refers to the limiting case of a complete reaction ($\zeta = 0$); the broken lines are calculated for the values of ζ shown. The points shown are calculated from the data[2] for the reaction $HPO_4^{2-} + OH^- \geq PO_4^{3-} + H_2O$. Those marked ○ correspond to an experiment in which the initial concentration (c_A) of Na_2HPO_4 was $0{\cdot}009464M(1/K_Tc_A = 2{\cdot}60)$, and those marked × to one where c_A was $0{\cdot}005644M(1/K_Tc_A = 4{\cdot}37)$.

titrant (B) is the hydroxyl ion. The reaction is,

$$HX + OH^- \rightleftharpoons H_2O + X^-$$

with

$$K = \frac{[X^-]}{[H^+][OH^-]} = \frac{K_a}{K_w}$$

where K_a is the normal dissociation constant of the acid, and K_w is the ionic product of the solvent water. If K_a is 10^{-9}, $K = 10^5$ at 25°, and if $c_A = 0{\cdot}1$, then $Kc_A = 10^4$, *i.e.*, a $0{\cdot}1M$ solution of an acid with $pK_a = 9$ should give a thermometric end-point almost as sharp as that of a strong acid, provided that the heat of neutralization is large enough. This is usually the case for weak protonic acids which have small heats of ionization. A usable end-point would also be expected at this concentration if $pK_a = 10$, but the end-point for still weaker acids must become indistinct in this concentration range. These conclusions have been amply confirmed by experiment on such acids as boric acid and the ammonium ion.[1]

The reduced enthalpogram for $\zeta = 1$ in Fig. 1 shows that at low values of β the limiting slope of the reduced enthalpogram does not become equal to that for the reduced enthalpogram with $\zeta = 0$ in the range $0 \leqslant \beta \leqslant 1$. The value of this limiting slope can be found by expanding (5):

$$\alpha = \frac{1}{\beta + \zeta + 1} + \frac{\beta}{(\beta + \zeta + 1)^3} + \text{higher terms.}$$

For small values of β only the first term need be considered and,

$$\lim_{\beta \to 0} (\alpha) = 1/(\zeta + 1).$$

This is the limiting slope of the reduced enthalpogram. That of the corrected experimental enthalpogram is, from this and equation (6),

$$-\frac{c_B}{(\zeta+1)}\Delta H_R .$$

Keily and Hume[5] proposed, in effect, that ΔH_R could be found from this limiting slope by equating $(\zeta + 1)$ with 1; this procedure clearly introduces an appreciable error if $\zeta \geqslant 10^{-2}$, and would not be applicable to weak complexes without modification. Dilke and Eley calculated the formation constant and enthalpy of formation for such complexes by first using the limiting slope of the enthalpogram to obtain ΔH_R, assuming $\zeta = 1$, and then combining this with calorimetric data near the equivalence point to obtain K. Such data are insensitive to ζ, and hence to K, when $\zeta < 10^{-3}$, and this method is limited to systems for which $10^{-3} < \zeta < 10^{-2}$, unless a successive approximation technique is used.

There are a number of more sophisticated methods available[4] for calculating K and ΔH_R from thermometric measurements, and Christensen, Izatt, Hansen and Partridge[2] have used such methods to analyse thermometric titration curves for the ionization of HSO_4^- and HPO_4^{2-}. To test the graphical method described here, reduced enthalpograms have been calculated from their results on HPO_4^{2-} at two concentrations; these are shown in Fig. 1. From their data they calculated a thermodynamic ionization constant, K_T, corrected to zero ionic strength, for the process

$$HPO_4^{2-} + OH^- \rightleftharpoons PO_4^{3-} + H_2O.$$

Their mean value for log K_T was $1{\cdot}61 \pm 0{\cdot}03$. Using this, and the initial titrant concentrations used[2], it is found that $\zeta = 2{\cdot}6$ and $4{\cdot}37$ respectively. Theoretical reduced enthalpograms for these ζ values are also shown in Fig. 1 and it is clear that the fit with the experimental data is not good. In fact the data which apparently correspond to $\zeta = 4{\cdot}37$ fit approximately to $\zeta = 2{\cdot}6$, and those nominally associated with $\zeta = 2{\cdot}6$ lie close to the curve for $\zeta = 1$. The discrepancies are caused by the fact that an equilibrium constant corresponding to the experimental ionic strength in the titration, rather than K_T, should have been used to calculate ζ. For the equilibrium above,

$$\log K_T = \log K + \log \frac{f_{PO_4^{3-}}}{f_{OH^-} f_{HPO_4^{2-}}}$$

If the simplest form of the Debye-Hückel equation for activity coefficients, $\log f_i = -0{\cdot}509\, z_i^2 \mu^{1/2}$, is applied to $0{\cdot}01M$ sodium dihydrogen phosphate,

$$\begin{aligned}\log K_T &= \log K - 2{\cdot}18\, \mu^{1/2} \\ &= \log K - 0{\cdot}37.\end{aligned}$$

The most concentrated solution used by Christensen *et al.* was approximately $0{\cdot}01M$, and the appropriate log K to use in calculating ζ can be obtained from the thermodynamic constant log K_T by adding $\sim 0{\cdot}37$ to it. This would reduce ζ from 2·6 to something close to 1. Quite obviously the reduced enthalpogram plot is very sensitive to ζ, and hence to K, for such weak acids.

Zusammenfassung—Es wird gezeigt, daß die Schärfe des Endpunktes einer thermometrischen Titration, in der die einfache Reaktion

$$A + B \rightleftharpoons AB$$

abläuft, von Kc_A' abhängt, wo K die Gleichgewichtskonstante der Reaktion und c_A' die Gesamtkonzentration des Titranden (A) im Reaktionsgemisch ist. Der Endpunkt ist scharf, wenn (1) die Reaktionsenthalpie nicht vernachlässigbar und (2) $Kc_A' > 10^3$ ist. Hieraus folgt, daß man beispielsweise eine 0,1 M Säure vom $pK_A = 10$ thermometrisch titrieren konnen sollte. Auch einige Aspekte der thermometrischen Titration bei $Kc_A' < 10^3$ werden erörtert.

Résumé—On montre que la netteté d'un point de fin de réaction dans un dosage thermométrique où se produit la réaction simple:

$$A + B \rightleftharpoons AB$$

dépend de Kc_A' où K est la constante d'équilibre pour la réaction et c_A' est la concentration totale de l'agent de titrage (A) dans le mélange réactionnel. Le point de fin de réaction est net si (1) la variation d'enthalpie dans la réaction n'est pas négligeable et (2) $Kc_A' > 10^3$. Ceci montre qu'il devrait, par exemple, être possible de doser un acide 0,1 M, $pK_A = 10$, en utilisant un point de fin de réaction thermométrique. On considère aussi quelques aspects de la titrimétrie thermométrique lorsque $Kc_A' < 10^3$.

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OXIDIMETRIC DETERMINATION OF INDIGO WITH IRON(III) AND HEXACYANOFERRATE(III)

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Summary—The use of iron(III) in sulphuric acid medium and of potassium hexacyanoferrate(III) in hydrochloric acid medium has been investigated for the oxidimetric determination of indigo and indigo sulphonic acid. Conditions have been established for the assay of the dye with iron(III) sulphate at 100° and with potassium hexacyanoferrate-(III) at room temperature.

INDIGO has been determined by oxidation with vanadium(V),[1] cerium(IV),[2] dichromate[3] and potassium iodate[4]. It has now been observed that indigo sulphonate is quantitatively oxidized when heated with excess of iron(III) sulphate in sulphuric acid. This reaction has been studied in detail and a method developed for the assay of indigo or indigo sulphonic acid. The reaction is of interest analytically because it is one of the few instances of an organic compound being quantitatively oxidized by iron(III). It is also of considerable significance in textile dyeing and laundering. If the water used in dyeing operations with indigo (and possibly other vat dyes) contains iron salts, the dyeing may not be uniform. If the laundering water is similarly contaminated, indigo dyeings may be partially bleached.

Flatow[5] carried out the direct titration of 0·0025–0·002*M* hexacyanoferrate(III) with 0·0005–0·0002*N* indigo sulphonic acid in potassium hydroxide medium. Flatow[6] has also titrated hexacyanoferrate(III) with indigo carmine solution in a sodium carbonate medium in connection with the estimation of uric acid. According to Welcher[7] the indigo carmine is oxidized in alkaline medium by potassium hexacyanoferrate(III) to form the pale yellow disulpho-dehydro-indigo, and not to isatin. The present work is concerned with the oxidation of indigo sulphonate in acid medium with hexacyanoferrate(III). It had been observed that the rate of oxidation of indigo by potassium hexacyanoferrate(III) at room temperature increases with increase in hydrochloric acid concentration. The reaction becomes very fast in 8*M* hydrochloric acid. In 3*M* hydrochloric acid the reaction takes about 60 min for completion, whereas in 6*M* hydrochloric acid it is complete within 1 min. In this reaction indigo is oxidized almost stoichiometrically to isatin; in sulphuric acid medium the reaction is very slow at all acidities tried from 0·25 to 2*M*.

It was also found by us that the rate of oxidation of indigo sulphonate by iron(III) in sulphuric acid was appreciable only at elevated temperature (100° is suitable) and that it decreases if the sulphuric acid concentration is increased above 1*M*, and increases as the ratio of iron(III) to indigo increases, reaching a maximum when this ratio is about 8.

EXPERIMENTAL

Reagents

Indigo sulphonate solution. About 1 g of pure indigo was sulphonated by digestion with 15 ml of concentrated sulphuric acid at 90° for 45 min. The reaction mixture was then cooled, diluted to

500 ml with conductivity water, and standardized by the vanadate procedure of Sastri and Gopala Rao. (The solution was 0·00763*M*. As the solution deteriorates on keeping, it had to be restandardized every day. The solution is preferably made with deionized water.)

Iron(III) and hexacyanoferrate(III), 0·1*M*. Prepared from salts of analytical reagent quality. The iron(III) sulphate solution was prepared in 0·5*M* sulphuric acid.

All other reagents were of analytical reagent quality.

Procedure with iron(III)

Adjust the acid concentration to 1*M* and the ratio of iron(III): indigo to 8–9 and heat the reaction mixture in a flask fitted with a Bunsen valve, in a boiling water-bath for 10 min. The reaction is complete when a clear golden yellow colour appears. When the reaction is complete, cool the mixture, add 3–5 ml of syrupy phosphoric acid, and titrate with a standard solution of potassium dichromate or sodium vanadate, using barium diphenylamine sulphonate as indicator. If sodium vanadate is used as reagent, add oxalic acid to the mixture to catalyse the indicator reactions. The number of moles of iron(III) consumed per mole of indigo is 4 ± 0·1, one mole of indigo being oxidized to two moles of isatin.

Typical results are shown in Table I.

TABLE I

Indigo sulphonate taken, *μmole*	Indigo sulphonate found, *μmole*
60·02	60·15
53·76	53·55
45·15	44·94
30·66	30·66
12·60	12·52
9·76	9·75
6·13	6·08

Procedure with hexacyanoferrate(III)

Treat 5 ml of indigo sulphonate solution with 5 ml of hexacyanoferrate(III) solution and sufficient concentrated hydrochloric acid to give an overall concentration of 6*M* hydrochloric acid on dilution to 35–40 ml. Set the mixture aside for a minute or two until the reaction is complete as shown by a clear golden yellow colour. Then dilute it with enough water to make the concentration of the acid 1*M*. To determine the amount of unreacted hexacyanoferrate(III), add 10 ml of 10% potassium iodide solution and 3 ml of 30% w/v zinc sulphate solution, and titrate the liberated iodine with 0·05*N* sodium thiosulphate. Standardize the hexacyanoferrate(III) solution by the same method.

Typical results are shown in Table II.

TABLE II

Indigo taken, *μmole*	Indigo found, *μmole*
34·33	34·35
41·19	41·17
45·30	45·33
46·96	46·95
53·55	53·58
63·01	62·95

One mole of indigo requires four moles of hexacyanoferrate(III). Oxalic acid, tartaric acid, citric acid, gum acacia, glucose, starch, dextrin, *etc.*, do not interfere in this procedure.

DISCUSSION

Interferences

The titrimetric determination of indigo sulphonate with potassium permanganate or cerium(IV) sulphate gives high values in the presence of organic substances such

as oxalic acid, citric acid, tartaric acid, glucose, starch and dextrin. These substances, except oxalic acid, do not interfere in the present method provided sodium vanadate is used for the determination of the iron(II) formed in the reaction between iron(III) and indigo. Potassium dichromate is unsuitable because during the titration of iron(II) the organic substances are also oxidized by an induced reaction. The presence of oxalic acid causes high results, the extent of interference increasing with increase in the concentration of oxalic acid. Further work is in progress to ascertain the cause of this interference.

Direct titration of hexacyanoferrate(III) with indigo sulphonic acid

Although indigo sulphonic acid is rapidly oxidized by hexacyanoferrate(III) in 8*M* hydrochloric acid, a direct titration has not been found possible, because of the difficulty experienced in locating the end-point visually and because of the difficulty of attainment of steady potentials if a potentiometric method is used. In the reverse titration of hexacyanoferrate(III) with indigo sulphonic acid in 8*M* hydrochloric acid medium, the potentials are stabilized quickly but the ratio of hexacyanoferrate(III) to indigo is irregular. However, the titration is possible with a visual end-point at room temperature, the self-colour of indigo sulphonic acid itself serving to mark the end-point. After all the hexacyanoferrate(III) disappears, the addition of a fraction of a drop of indigo solution imparts a green colour to the titration mixture; in such titrations, an average of 3·76 moles of hexacyanoferrate(III) is required for the oxidation of 1 mole of indigo. Although the oxidation of indigo does not proceed to isatin stoichiometrically, this titration can still be used because of the near constancy ($\pm 1{\cdot}5\%$) of the ratio of hexacyanoferrate(III) to indigo.

This reaction is one of the few instances of hexacyanoferrate(III) being used as an oxidimetric reagent in acid medium. According to Berka, Vulterin and Zýka,[8] most oxidations with hexacyanoferrate(III) are carried out in alkaline medium.

Zusammenfassung—Die Verwendung von Eisen(III) in schwefelsaurer und von Kaliumhexacyanoferrat(III) in salzsaurer Lösung zur oxidimetrischen Bestimmung von Indigo und Indigosulfonsäure wurde untersucht. Es wurden Arbeitsbedingungen festgelegt für die Gehaltsbestimmung der Farbe mit Eisen(III) sulfat bei 100° und mit Kaliumhexacyanoferrat(III) bei Zimmertemperatur.

Résumé—On a étudié l'emploi du fer (III) en milieu acide sulfurique et du ferricyanure de potassium en milieu acide chlorhydrique pour le dosage oxydimétrique de l'indigo et de l'acide indigo sulfonique. On a établi les conditions de dosage des colorants avec le sulfate de fer (III) à 100° et avec le ferricyanure de potassium à température ordinaire.

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SHORT COMMUNICATIONS

Milligram determination of aromatic amines and phenols with *N*-bromosuccinimide

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THE usual bromination reactions[1-5] employed for the determination of a large number of aromatic amines and phenols have been found to be inapplicable to compounds such as *p*-aminobenzoic acid, *p*-nitroaniline and aniline at higher temperature. The reaction takes a long time in many cases and does not give accurate results.

Taking advantage of the rapid bromination reaction of *N*-bromosuccinimide with different aromatic compounds,[6] we have developed a quantitative and accurate method for the milligram determination of aromatic amines and phenols. A 2–4 mg sample is dissolved in a hydrochloric–acetic acid mixture and treated with a known excess of the *N*-bromosuccinimide solution. The reaction is allowed to proceed for about 10 min and the excess of the reagent is determined iodometrically. A blank determination is made under identical conditions and a correction for it is applied.

EXPERIMENTAL

Reagents

N-*Bromosuccinimide, ca.* 0·01*M*. Dissolve about 0·2 g of reagent in hot distilled water, cool the solution and dilute it to 100 ml with distilled water. The solution should be freshly prepared before use, and standardized iodometrically.[7]

Sample. Weigh accurately 20–40 mg of sample, dissolve it in the minimum amount of 4*M* hydrochloric acid (for amines) or water, or 4*M* sodium hydroxide (for phenols), and dilute to 50 ml with distilled water. Alternatively use 2–4 mg of sample, without dilution.

General procedure

Transfer 5 ml of the sample solution to a 100-ml iodine flask, add 5 ml of 4*M* hydrochloric acid, 5 ml of glacial acetic acid, and 10 ml of *N*-bromosuccinimide solution, stopper and shake well. After about 10 min, add about 1 g of potassium iodide and titrate against 0·025*N* sodium thiosulphate with starch (1% aqueous solution) as indicator. The same procedure is followed for a blank, and the difference in the titrations is used for the calculation:

$$\text{Amine content} = \frac{MVC}{n}\ \text{mg}$$

where M = molecular weight of sample,
V = volume (in ml) of *N*-bromosuccinimide solution used in the reaction,
C = molarity of the *N*-bromosuccinimide solution.
and n = number of moles of *N*-bromosuccinimide required per mole of the sample for complete reaction.

RESULTS AND DISCUSSION

Amines

For the quantitative determination of amines, aniline was chosen as the representative compound. At first, direct titration of the aniline sample in acidic medium against *N*-bromosuccinimide, with Methyl Red as indicator, was tried, but the end-point was not very sharp and the results obtained were about 12% low.

The indirect titrimetric method—addition of a known excess of *N*-bromosuccinimide solution and iodometric titration of the excess of reagent—was next tried. This procedure gave sharp end-points and was specially suited for the determination of coloured compounds such as nitroanilines and nitrophenols and also for compounds which require a moderate reaction time. It was therefore used in all the subsequent determinations. With some loss of accuracy, as little as 0·5 mg of aniline could be determined (Table I).

TABLE I.—DETERMINATION OF ANILINE BY INDIRECT TITRATION

Sample, *mg**	Aniline found, *mg*	Error, %
5·02	4·86, 4·85, 4·86	−3·2
3·50	3·42, 3·42, 3·41	−2·4
2·50	2·46, 2·45, 2·45	−1·8
1·50	1·48, 1·48, 1·48	−1·3
1·00	0·97, 0·96, 0·97	−3·5
0·50	$0{\cdot}47_3$, $0{\cdot}47_8$, $0{\cdot}47_3$	−5·5

* In each case, 3 aliquots taken.

In general too large an excess of the brominating agent causes low results, perhaps because loss of bromine by volatilization may be greater in the blank. The recommended procedure gives reasonably accurate results with *p*-nitroaniline, which cannot be determined by the classical bromination method. Determination of toluidines presented difficulty in judging the end-point; a continuing consumption of the reagent was noticed on allowing the reaction mixture to stand. However, *o*-toluidine could be determined with less difficulty. The abnormal behaviour of toluidines may be due to partial bromination of the methyl group along with bromination of the benzene ring. In the case of benzidine the expected derivative is a tetrabromo compound but the amount of the brominating reagent consumed varied continuously with time and no proper stoichiometry could be obtained. Similarly in mono- and dimethylanilines a constant end-point could not be obtained.

The presence of carboxylic and sulphonic acid groups in the aniline molecule retards the speed of

TABLE II.—DETERMINATION OF AROMATIC AMINES

Sample	Taken, *mg**	Reaction time, *min*	Equivalents of NBS†	Found, *mg*	Error, %
m-Nitroaniline	3·00		2	2·93	−2·2
				2·91	−3·0
				2·91	−3·0
o-Nitroaniline	2·52		2	2·46	−2·4
				2·46	−2·4
				2·46	−2·4
p-Nitroaniline	3·00		2	2·94	−2·0
				2·95	−1·7
				2·95	−1·7
o-Toluidine	3·00		2	3·12	+4·0
				3·10	+3·3
				3·11	+3·7
Sulphanilic acid	4·00	5	3	3·80	−5·0
				3·81	−4·8
				3·80	−5·0
p-Aminobenzoic acid	3·22	8	3	3·16	−1·9
				3·16	−1·9
				3·17	−1·6
m-Aminobenzoic acid	3·12	8	3	3·09	−1·0
				3·08	−1·3
				3·09	−1·0
o-Aminobenzoic acid	2·50	2	3	2·44	−2·4
				2·43	−2·8
				2·43	−2·8
Diphenylamine	2·00	10	6	1·87	−6·5
				1·87	−6·5
				1·87	−6·5

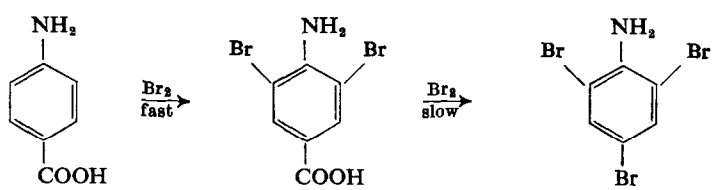
* In each case, 3 aliquots taken.
† *N*-Bromosuccinimide.

TABLE III.—DETERMINATION OF PHENOLS

Sample	Taken, *mg**	Reaction time, *min*	Equivalents of NBS†	Found, *mg*	Error, %
Phenol	2·00		3	2·03	+1·5
				2·04	+2·0
				2·03	+1·5
o-Nitrophenol	2·12		2	2·07	−2·4
				2·08	−1·9
				2·08	−1·9
p-Nitrophenol	1·90		2	1·87	−1·6
				1·86	−2·1
				1·86	−2·1
m-Nitrophenol	2·22		2	2·16	−2·7
				2·15	−3·2
				2·15	−3·2
p-Chlorophenol	1·56		2	1·49	−4·5
				1·49	−4·5
				1·49	−4·5
o-Hydroxybenzoic acid	1·85	5	3	1·78	−3·8
				1·77	−4·3
				1·77	−4·3
m-Hydroxybenzoic acid	1·65		3	1·61	−2·4
				1·61	−2·4
				1·60	−3·0
p-Hydroxybenzoic acid	1·90		3	1·87	−1·6
				1·88	−1·1
				1·88	−1·1
Resorcinol	2·12	5	3	2·13	+0·5
				2·13	+0·5
				2·11	−0·5
α-Naphthol	2·00		2	2·05	+2·5
				2·06	+3·0
				2·05	+2·5
β-Naphthol	2·10		1	2·00	−4·8
				2·00	−4·8
				2·00	−4·8

* In each case, 3 aliquots taken.
† *N*-Bromosuccinimide.

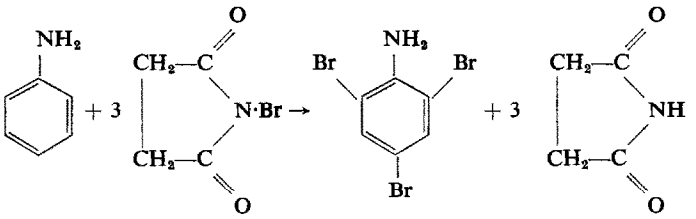
the reaction to a great extent, which may be explained by the fact that the reaction proceeds faster in the first step whereas the last step is slow.



Diphenylamine also reacts slowly. Tertiary amines such as dimethylaminobenzaldehyde and tetramethyldiaminobenzophenone give inconsistent results, probably due to the effect of the methyl groups. Results obtained with a few of the compounds are given in Table II.

The bromination reaction with *N*-bromosuccinimide is almost instantaneous with some amines and phenols, but in some cases the reaction is not so fast and the reaction takes about 10 min to reach completion. In a general procedure for the analysis of an unknown sample the reaction time allowed should be 10 min.

Taking aniline as an example, the bromination reaction may be represented by the equation



The number of bromine atoms entering the molecule may differ in different compounds but must be known for the determination; however, the bromination reactions of aromatic amines and phenols are well established by the usual bromination methods with bromate–bromide mixture as reagent.[3–5]

Phenols

In the determination of phenols, we observed that the presence of a nitro group *meta* or *para* to the phenolic group does not hinder the reaction, while a carboxyl group in the *ortho* position makes the reaction very slow, possibly because of hydrogen-bonding between the hydroxyl and carboxyl groups. In the case of dihydric phenols, the presence of hydroxyl groups *meta* to each other does not cause any trouble, but *ortho* and *para* dihydroxy groupings lead to inconsistent results. Probably the compounds undergo slow oxidation as well as or instead of bromination. Similar behaviour was noticed in the case of quinhydrone. Results obtained with some of the phenolic compounds are given in Table III.

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Summary—A simple and rapid method has been developed for the determination of milligram amounts of aromatic amines and phenols. An aliquot containing 2–4 mg of sample is dissolved in a mixture of hydrochloric and acetic acids and allowed to react with *N*-bromosuccinimide, the excess of which is determined iodometrically after the reaction is over. The reaction time varies from 1–10 min and the absolute error generally is negative, ranging from −1 to −4%.

Zusammenfassung—Eine einfache und schnelle Methode zur Bestimmung von Milligrammengen aromatischer Amine und Phenole wurde entwickelt. 2–4 mg Probe werden in einer Mischung aus Salzsäure und Essigsäure gelöst und mit N-Bromsuccinimid zur Reaktion gebracht; dessen Überschuß wird nach Ablauf der Reaktion jodometrisch bestimmt. Die Reaktionszeit leigt zwischen einer und zehn Minuten und der Absolutfehler ist im allgemeinen negativ, zwischen −1 und −4%.

Résumé—On a élaboré une méthode simple et rapide pour le dosage de quantités d'amines aromatiques et de phénols de l'ordre du milligramme. On dissout un prélèvement contenant 2–4 mg d'échantillon dans un mélange d'acides chlorhydrique et acétique et le fait réagir avec le N-bromosuccinimide, dont l'excès est dosé par iodométrie après fin de réaction. Le temps de réaction varie de 1 à 10 mn et l'erreur absolue est généralement négative, allant de −1 à −4%.

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Microchemical detection of isocyanides

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RECENT surveys on α-addition reactions[1] and synthesis methods[2] indicate considerable interest in the use of isocyanides in organic chemistry. The characteristic and unpleasant odour of an iso-cyanide gives such a sensitive and rapid method of identification[3] it is not surprising that only one chemical detection method was found in the literature. Smith and Kalenda[3] mentioned that the colour test of Pertusi and Gastaldi[4] is useful for detecting the presence of isocyanides in reaction mixtures but gave no experimental details. This particular test is based on the oxidation of benzidine to benzidine blue by copper(II) acetate when a suitable complexing agent is present. It is well-known for its adaption to the detection of hydrogen cyanide.[5,6] We studied several aromatic amine—metal ion redox systems and report in this paper the microchemical detection of isocyanides on filter paper or in tubes of silica gel with benzidine acetate–copper(II) acetate or *p,p'*-tetramethyldiamino-diphenylmethane–copper(II) sulphate reagents.

EXPERIMENTAL

Reagents

Benzidine acetate—copper(II) acetate reagent (benzidine reagent). Mix, just before use, equal volumes of (*a*) aqueous cupric acetate solution, 2·86 g/l and (*b*) 675 ml of benzidine acetate solution (saturated at room temperature) mixed with 525 ml of water. The stock solutions are best stored separately in well stoppered, dark bottles.

Tetrabase—copper(II) sulphate reagent (tetrabase reagent). Mix equal volumes of solutions of (*a*) 100 mg of tetrabase (*p,p'*-tetramethyldiaminodiphenylmethane) and 500 mg of salicylic acid in 100 ml of acetone and (*b*) 1·5 g of copper(II) sulphate in 100 ml of water.

Apparatus

Silica gel tubes. A 2 × 9-cm test-tube with a capacity of about 12 ml was fitted, by means of a 19/38 standard taper joint, with an adapter supporting a side-arm air inlet and a length of glass tubing that extended to within 5 to 10 mm of the bottom of the test tube (Fig. 1). Silica gel tubes[7–9] were connected by a short length of rubber tubing to the upper end of the glass tubing. Vapours from the test-tube were drawn through the detector tube by compressing a rubber bulb.

Procedure with silica gel tubes

Samples of varying amounts of the pure isocyanides dissolved in methylene chloride (1–50 μl, 0·0004–0·002*M*) were measured with disposable pipettes and placed in the test apparatus described above. When an unimpregnated silica gel detector tube is used, the isocyanide vapour is collected on the silica gel, the detector tube is removed from the apparatus, and the silica gel is moistened with a drop of either reagent. The appearance of a blue colour is a positive test for isocyanide. A blue colour is produced directly when the isocyanide vapour is sampled by drawing it through a silica gel tube impregnated with tetrabase reagent. Such a detector tube is prepared from silica gel impregnated with copper(II) sulphate pentahydrate, *p,p'*tetramethyldiaminodiphenylmethane and salicyclic acid.[10] A red dye (diazotized anthranilic acid coupled with diethylaniline) is also added to mask the blue colour of the copper(II).

The n-butyl, s-butyl, and t-butyl isocyanides were synthesized by reacting tosyl chloride, quinoline and the corresponding n-alkyl formamide.[2,11]

RESULTS

Spot-tests on filter papers

The isocyanide test was initially developed as a spot-test on filter paper. Several kinds of paper were compared since the sensitivity of certain spot-tests can be increased by using the proper filter paper.[12]

Benzidine reagent. In each test, 10 μl of the benzidine reagent were placed on the filter paper, and 10 μl of methylene chloride containing 0·18 μg of n-butyl isocyanide were added. On the basis of the intensity of the blue colour produced the papers were grouped into three categories:

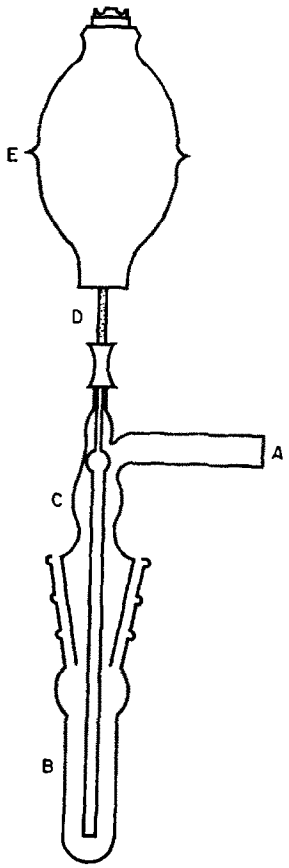

FIG. 1.—Test apparatus.
A—Air inlet; B—2 × 9-cm test-tube with 19/38 standard taper joint; C—adapter; D—silica gel tube; E—rubber aspirator bulb with one-way valve.

Most sensitive (positive test)	*Least sensitive* (negative test)
Detector paper*	Whatman 30
S&S† 589	Whatman 1
Whatman‡ 3	Whatman 4
	Whatman 40
Intermediate sensitivity (doubtful test)	Whatman 41
Whatman 120	Whatman 2
Whatman 31	S&S 576
Whatman 5	S&S 410
S&S 597	S&S 602
S&S 604	S&S 589 Blue ribbon
	S&S 589 Black ribbon

Tetrabase reagent. The tetrabase reagent (10 μl) gave a pale blue colour with 5 μg of n-butyl isocyanide on the paper tape impregnated with Parez® 607 resin (about the same intensity as that given by 0·5 μg of n-butyl isocyanide with the benzidine reagent). Similar results were found with the Whatman 120 paper. The blue colour with tetrabase reagent was stable, whereas that with benzidine faded within a few minutes.

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* A high α-cellulose-content paper impregnated with about 0·8% of Parez® (American Cyanamid Co.) resin.[18]

† Carl Schleicher & Schuell Co., Keene, New Hampshire, U.S.A.

‡ W. and R. Balston, Ltd., Maidstone, England.

Tests on the silica gel tubes

The sensitivity of isocyanide detection was improved by the use of silica gel detector tubes (Table I).

TABLE I.—COLORIMETRIC DETECTION OF ISOCYANIDES IN THE VAPOUR STATE WITH SILICA GEL TUBES

Technique	Amount of isocyanide tested*		
	n-Butyl	s-Butyl	t-Butyl
Sampling through silica gel tubes followed by addition of benzidine reagent	0·15 μg, definite light blue 0·06–0·12 μg, faded rapidly	0·09 μg, definite test 0·06 μg, faint test	0·12 μg, definite test 0·09 μg, faint test
Sampling through silica gel tubes impregnated with tetrabase reagent	0·12 μg, definite blue colour 0·06–0·09 μg, faint test	0·09 μg, definite test 0·06 μg, faint test	0·09 μg, definite test 0·06 μg, faint test

* It is assumed that all of the isocyanide placed in the test apparatus was sampled.

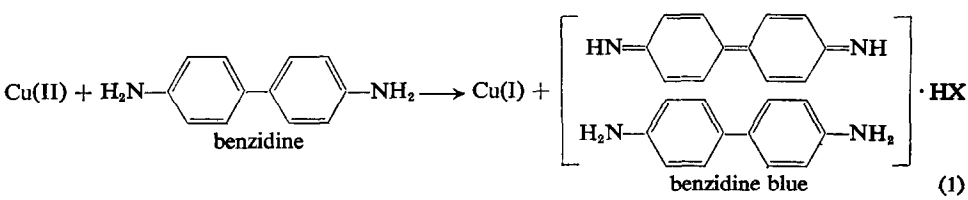
About 0·1 μg of the butyl isocyanides was easily detected. The colour formed in the benzidine test faded rapidly after 1–5 min. The blue colour formed in tetrabase impregnated tubes was stable, but after prolonged standing (about 2 hr) all the impregnated tubes, including the blank controls, turned deep blue.

Interferences

Substances that interfere in the detection of hydrogen cyanide also interfere in the detection tests for isocyanides.[5] They include volatile oxidizing or reducing agents and certain electrophiles or acids. For example, with the tetrabase reagent, we confirmed that strong acids give a yellow colour and sulphides give a brown colour.

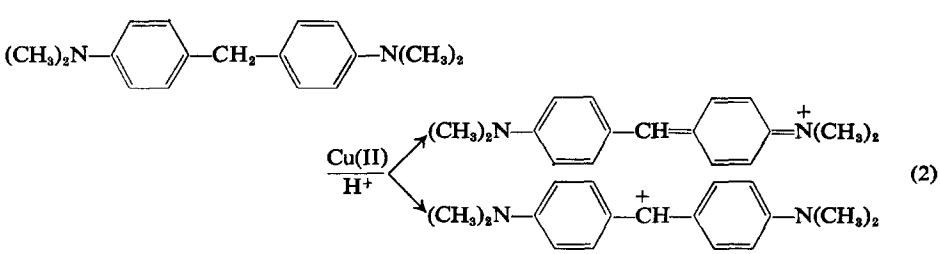
DISCUSSION

The mechanisms of the colorimetric tests for alkyl isocyanides with the benzidine or the tetrabase reagent are probably similar to those described for the well-known methods for cyanide. The benzidine test, sensitive to 0·25 μg of cyanide at a limit of dilution of 1 in 200,000,[5] is one of the easiest and most sensitive methods for detecting cyanide.[6] This reaction, equation (1), takes place because the oxidation potential of copper(II) is increased by the removal of copper(I) as an insoluble complex.



(1)

The coloured oxidation product of tetrabase contains the quinoidal or carbonium cation, equation (2). Only the salts of these cations are blue, and



(2)

when they are exposed to ammonia vapour the colourless carbinol base is formed; with the addition of acetic acid, the blue colour reappears.

The benzidine test can be modified by the use of other amines such as *o*-tolidine, *p*-diaminodiphenylamine, *p*-aminodimethylaniline, or *o*-dianisidine.

After this work had been terminated, Feigl and Anger[14] published a procedure for hydrogen cyanide and cyanogen in which the benzidine and copper(II) acetate were replaced by tetrabase and copper(II) ethyl acetoacetate. The detection limit was 1 μg of hydrogen cyanide. This reagent combination should also be effective with the alkyl isocyanides, but it was not tested.

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Summary—Microgram quantities of isocyanides may be easily detected on filter paper or in tubes of silica gel by using benzidine acetate–copper(II) acetate or *p,p'*-tetramethyldiaminodiphenylmethane–copper(II) sulphate reagents. Interferences include those substances which are known to interfere in the use of the same reagents for the detection of hydrogen cyanide. The lowest amount of n-, s-, or t-butyl isocyanide detectable is approximately 0·1 μg.

Zusammenfassung—Mikrogrammengen von Isonitrilen lassen sich auf Filtrierpapier oder in Kieselgelrohrchen leicht nachweisen mit Benzidinacetat-Kupfer(II) acetat oder *p,p'*-Tetramethyldiaminodiphenylmethan-Kupfer(II) sulfat als Reagentien. Es stören die Substanzen, die auch beim Nachweis von Blausäure mit diesen Reagentien stören. Die kleinste nachweisbare Menge n-, s- oder t-Butylisonitril ist etwa 0,1 μg.

Résumé—On peut aisément détecter des quantités de carbylamines de l'ordre du microgramme sur papier filtre ou dans des tubes en gel de silice en utilisant des réactifs à l'acétate de benzidine-acétate de cuivre(II) ou au *p,p'*-tétraméthyldiaminodiphénylméthane-sulfate de cuivre(II). Les interférences comprennent les substances qui sont connues comme gênantes lors de l'emploi des mêmes réactifs pour la détection de l'acide cyanhydrique. La plus faible quantité de *n*-, *s*- ou *t* butylcarbylamine détectable est approximativement de 0,1 μg.

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p-Aminoacetophenone as a reagent for the colorimetric determination of cerium(IV)

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THERE exist in the literature only a few methods for the colorimetric determination of cerium(IV). Sandell[1] and Medalia and Byrne[2] utilized the yellow colour of cerium(IV) solutions. Telep and Boltz[3] used the carbonato-complex of cerium(IV) which absorbs at 304 mμ. Gordon and Feibush[4] developed an indirect colorimetric determination of cerium(IV) in which an excess of iron(II) was added to it and the excess of iron(II) was complexed with 1,10-phenanthroline. Recently Sarma and Dieter[5] determined cerium(IV) in the presence of rare earths by means of its colour reaction with sulphanilic acid, but the colour is very unstable and many oxidizing agents and coloured metal ions interfere.

p-Aminoacetophenone has been used as a reagent for the detection[6] and determination[7] of palladium. Since then no-one appears to have used this compound for analytical purposes. We have observed that cerium(IV) gives a purple colour with *p*-aminoacetophenone and that cerium(IV) can be detected with an identification limit of 1·0 μg even in the presence of rare earths and some oxidizing agents and coloured ions. The dilution limit is 1 in 50000. We have been able to use this reaction for the colorimetric estimation of cerium(IV). This method is found to be more accurate and precise and with less interferences than the existing methods.

EXPERIMENTAL

Reagents

Cerium(IV) sulphate solution. Prepared and standardized according to Willard and Young,[8] and suitably diluted with 0·5*N* sulphuric acid.

p-*Aminoacetophenone solution*, 0·5%. The compound is dissolved in hot dilute hydrochloric or sulphuric acid, cooled, and diluted with redistilled water, to yield a 0·01*N* acid solution.

Buffer solutions. Clark and Lubs buffer mixtures of potassium chloride and hydrochloric acid.

Procedure

Take a known volume of cerium(IV) solution of unknown concentration in a 25-ml volumetric flask. Add 15·0 ml of buffer solution (pH 1·6) and 2·0 ml of the reagent solution, and dilute to the mark with redistilled water. Mix thoroughly, and measure the absorbance exactly 3 min after addition of the reagent.

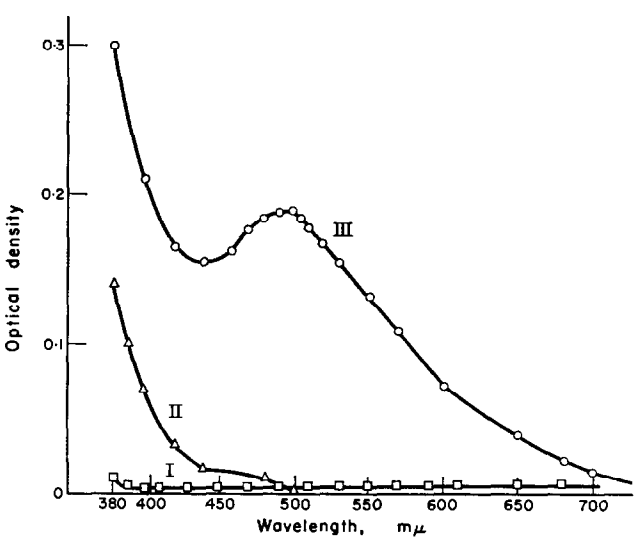

FIG. 1.—Absorption spectra of cerium(IV), *p*-aminoacetophenone, and their reaction product at pH 1·6.
I—*p*-Aminoacetophenone (0·04%); II—0·0002*M* Cerium(IV); III—reaction product.

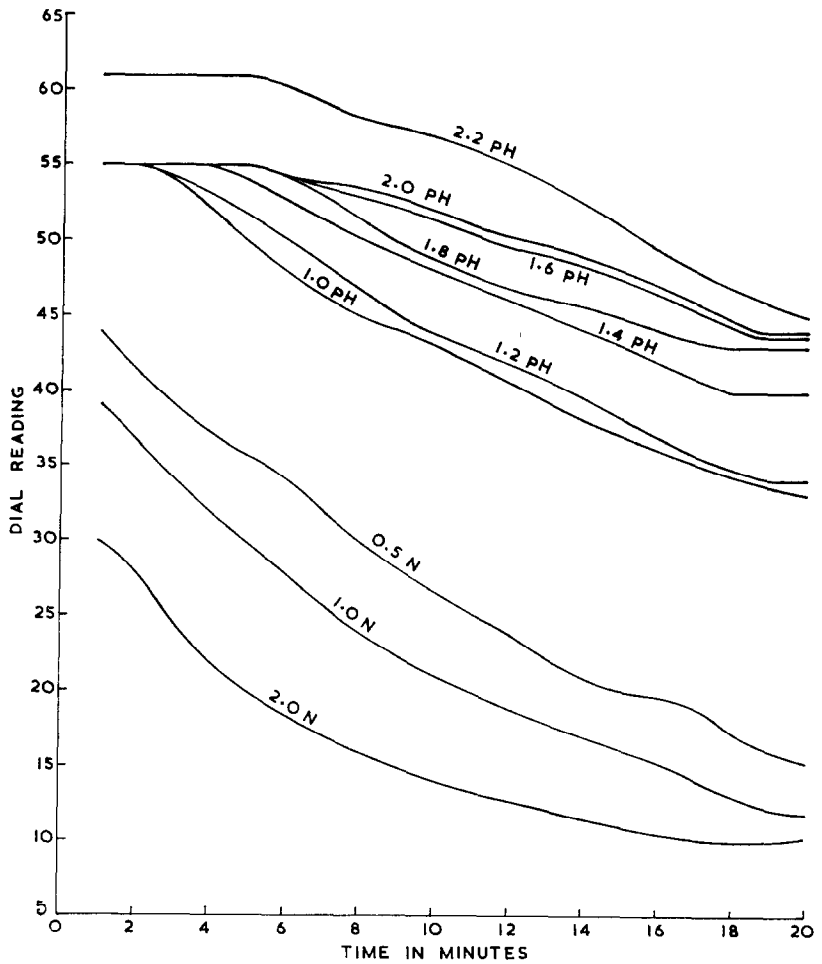

FIG. 2.—Stability of colour at various acidities.

Beer's law is obeyed over the range 14–350 μg of cerium per 25 ml of solution. A green filter (EEL 623 or 624) should be used, or a wavelength of 500 mμ. The error is about 1% over the range quoted. The absorption spectrum is shown in Fig. 1.

RESULTS AND DISCUSSION

When 1·0 ml of 0·0025*M* cerium(IV), 15 ml of buffer solution and 2·0 ml of the reagent solution were mixed and diluted to 25·0 ml, it was found that the absorbance, measured within 5 min, was independent of pH over the range 1·4–1·6, see Fig. 2. At pH > 1·8 the solution rapidly becomes turbid, probably because of hydrolysis of the cerium(IV). Even if the acidity is increased the coloured product seems to be stable for 5 min at most. Hence a pH of 1·6 was chosen as suitable and absorbances were measured 3 min after mixing the reagents.

When the ratio of the reagent and cerium(IV) concentrations was varied from 1 to 300 and the absorbances were measured, the absorbance increased slightly with increase of the ratio from 1 to 5, remained constant up to a ratio of 120 and thereafter decreased again. Hence the reagent should be present in from 10- to 100-fold excess.

The absorbance decreases as the temperature is raised and at above 50° the solution turns turbid immediately.

Interferences

Oxidizing agents such as permanganate, bismuthate and lead dioxide interfere by giving colour reactions with the reagent, though the last two could be filtered off before the reagent is added. Periodate causes turbidity in the solution. Hence these ions should be absent. Bromate does not interfere if present in amounts less than twenty times that of the cerium(IV). Vanadate and persulphate do not interfere at all. Bromate, dichromate and periodate give a brown colour with the reagent at higher temperatures.

Among the coloured ions, chromium(VI) does not interfere if its concentration is less than that of the cerium. Cobalt, nickel and copper do not interfere even if present in amounts ten times that of the cerium. Aluminium, calcium, zinc, thorium, zirconium, thallium, manganese(II), tantalum, and rare earths do not interfere. Chloride does not interfere but nitrate decreases the intensity of the colour.

Since the oxidizing agents which interfere give nearly the same colour as that obtained with cerium(IV), the coloured species produced is probably an oxidation product of the reagent. Further work is in progress on the mechanism of the oxidation of the compound.

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Summary—With a solution of *p*-aminoacetophenone, cerium(IV) gives a purple colour which can be used for its detection and determination. The limits of identification and dilution are 1·0 μg and 1 in 50000 respectively. Beer's law is obeyed in the range 14–350 μg. The colour is stable for only 5 min and measurements of absorbance must be made quickly. The interferences are fewer than with existing methods.

Zusammenfassung—Mit einer Lösung von *p*-Aminoacetophenon gibt Cer(IV) eine Purpurfärbung, die zu seinem Nachweis und zu seiner Bestimmung dienen kann. Nachweis- und Verdünnungsgrenze sind 1,0 μg bzw. 1:50 000. Das Beersche Gesetz gilt bei 14–350 μg. Die Färbung ist nur 5 min stabil; die Extinktionsmessungen müssen schnell vonstatten gehen. Es gibt weniger Störungen als mit den bekannten Methoden.

Résumé—Le cérium (IV) développe avec une solution de *p*-amino-acétophénone une coloration pourpre qu'on peut utiliser pour sa détection et son dosage. Les limites d'identification et de dilution sont de 1,0 μg et 1 dans 50,000 respectivement. La loi de Beer est respectée dans le domaine 14-350 μg. La coloration est stable pendant 5 mn seulement et les mesures d'absorption doivent être effectuées rapidement. Les interférences sont moins nombreuses qu'avec les méthodes existantes.

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Some solvent effects on the solvent extraction of 8-quinolinol

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UNTIL recently, the study of the solvent extraction of metal ions with chelating agents has been concentrated on the chemical formation of the metal chelates rather than on their properties once they have been formed.

Some work has been reported on the role of the solvent on the chelate extraction process.[1-11] In an earlier paper[12] dealing with the determination of the distribution constants of 8-quinolinols and their copper(II) chelates, we were able to explain the solvent effects largely in terms of non-specific interactions. Correlated parameters of importance included mutual solubility of phases, dielectric constant, and solubility parameter of the solvent.

An important exception among the solvents studied was chloroform, in which distribution constants were found to be significantly higher than expected. Similar behaviour for β-diketones in chloroform–water systems had been noted earlier.[2,8] Since the hydrogen-bonding ability of chloroform might well be responsible for the high distribution constants observed it was decided to determine the distribution behaviour of 8-quinolinol between water and a series of substituted aliphatic hydrocarbon solvents having electron withdrawing groups which might impart hydrogen-bonding ability.

EXPERIMENTAL

Reagents

8-Quinolinol (Eastman Organic Chemicals) was recrystallized from boiling absolute ethanol. The melting point of the recrystallized product, after drying *in vacuo* in a desiccator, was 71·5–73·0°.

Nitro- and chloronitroalkanes (Commercial Solvents Corporation) were washed several times with deionized water and with the corresponding buffered aqueous phase used in the distribution experiments. The nitroalkanes, with densities close to that of water, were used in carbon tetrachloride (J. T. Baker, Analytical Reagent) solution. The amount of nitroalkane in the mixture after washing was calculated, taking into account its solubility in water.

1-Bromo-3-chloropropane, *1,2-dichloroethane*, *dibromomethane*, *and bromochloromethane*, were commercial-grade solvents (Dow Chemical Company); they were purified by distillation and washing with deionized water and the corresponding buffered aqueous phase used in the distribution experiments.

1-Bromobutane was practical grade from Matheson, Coleman and Bell and was purified in a similar way.

All other solvents were of analytical grade and were washed several times with water and buffer solution. Finally, after washing, all solvents were presaturated with the buffered aqueous phase.

The aqueous phase was buffered with sodium dihydrogen phosphate and sodium hydroxide and maintained at ionic strength 0·10 ± 0·02.

All other chemicals were of analytical reagent quality. All experiments were carried out at 25·0 ± 0·2° and the reported values are averages of at least three separate determinations. The experimental procedure and apparatus used in the determination of concentrations are described in a preceding paper.[12]

RESULTS AND DISCUSSION

Distribution of 8-quinolinol between some halogenated hydrocarbon–water pairs

In Table I are listed the distribution-constant values for 8-quinolinol expressed in terms of molarity ratios, K_D, and mole fraction ratios, K_D^x. From the values of K_D, the practical advantage of using an organic solvent having a high molecular weight and density can be seen. For example, the K_D in bromochloromethane is almost 20% higher than the corresponding chloroform value though the K_D^x values are almost the same. Again, despite the lower K_D^x value, the K_D in dibromomethane is slightly larger than that in chloroform.

K_D^x values provide a more rational basis for evaluation of the role of the solvent inasmuch as they provide a comparison of equal numbers of molecules. Of all the solvents studied, chloroform appears to be the best. Although not many examples are presented, there seems to be a trend towards increasing K_D^x with introduction of bromine atoms.

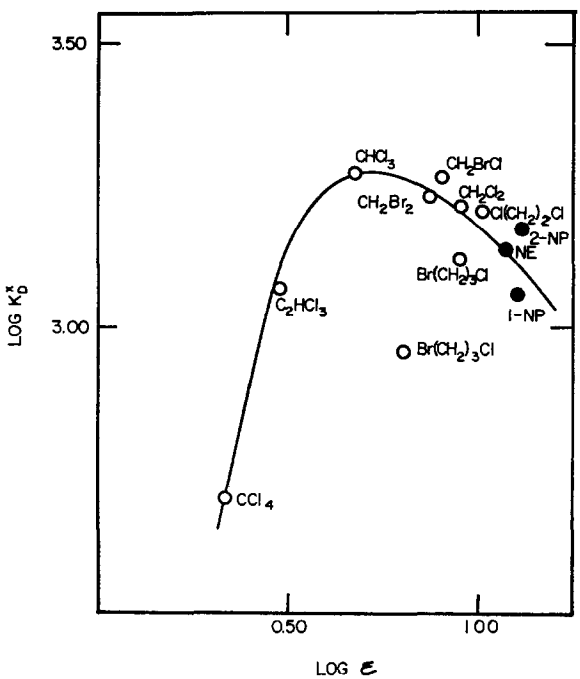

FIG. 1.—Distribution of 8-quinolinol in a series of halogenated hydrocarbon–water systems; effect of dielectric constant of pure solvent.
Values for nitroalkanes–CCl_4(1:1 mole mixture, $10^{-1}M$ 8-quinolinol) are added for comparison. *NE*: Nitroethane; 1-*NP*: 1-Nitropropane; 2-*NP*: 2-Nitropropane

TABLE I.—THE DISTRIBUTION OF 8-QUINOLINOL BETWEEN A SERIES OF HALOGENATED HYDROCARBONS AND THE AQUEOUS PHASE (pH = 6·5–7·0; μ = 0·10) AT 25·0 ± 0·2°C.

Organic solvent	Dielectric constant	Solubility* parameter	Distribution constants	
			K_D	K_D^x
Dichloromethane	9·1	9·7	377	1330
1,2-Dichloroethane	$10{\cdot}3_6$	9·9	359	1607
Chloroform	4·8	9·3	433	1915
Trichlorethylene	3·42	9·3	240	1205
Carbon tetrachloride	2·23	8·6	116	621·4
Bromobutane	6·5	8·7	159	949
Dibromomethane	7·7	10·2	449	1743
Bromochloromethane	$8{\cdot}0_7$	10·2	503	1874
1-Bromo-3-chloropropane	9·43	—	310	1703
n-Hexane†	1·9	7·3	21·2	153·8

* The values of solubility parameters have been taken from: (*a*) J. H. Hildebrand and R. L. Scott, *Regular Solutions*, Prentice-Hall, 1962; (*b*) *Bromine and Brominated Products Handbook*, Dow Chemical Company, Midland, Michigan, except for bromochloromethane which was calculated from its latent heat of vaporization at 25°.

† The value for n-hexane is included for comparison.

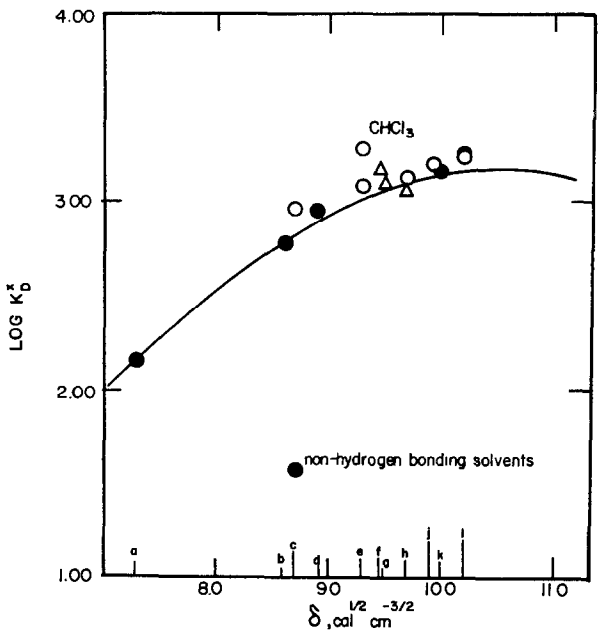

FIG. 2.—Distribution of 8-quinolinol between a series of halogenated hydrocarbon–water systems; effect of solubility parameter of pure solvent.
Values for nitroalkane-CCl_4(Δ) added for comparison (1:1 mole mixture, $10^{-1}M$ 8-quinolinol in organic phase.)

a: n-Hexane
b: Carbon tetrachloride
c: Bromobutane
d: Toluene
e: Chloroform
f: 2-Nitropropane
g: 1-Nitropropane
h: Nitroethane and dichloromethane
j: 1,2-Dichloromethane
k: Dichlorobenzene
l: Bromochloromethane and dibromomethane

Even though there exists no simple and general quantitative relation between distribution constants and properties of solvents, the empirical correlation of distribution data and the dielectric constant as well as the solubility parameter of the pure solvent show interesting trends. Figure 1 shows a plot of log K_D^x *vs.* the log of the dielectric constant of the pure solvent (ε). Confirming earlier observations,[12] the plot is somewhat parabolic in shape. The maximum appears close to the value for the dielectric constant of 8-quinolinol (4·73).[13]

Any correlation based on solubility parameter alone, as introduced by the regular solution theory, focuses attention on non-specific interactions. A plot of log K_D^x *vs.* the solubility parameter of the pure solvent is shown in Fig. 2. The solid line has been calculated with the help of the equation

$$2{\cdot}3RT \log K_D^x = V_c[(\delta_c - \delta_{aq})^2 - (\delta_c - \delta_0)^2]$$

where δ_c and V_c are the solubility parameter and molar volume respectively of the distributing species, and δ_{aq} and δ_0 the solubility parameter of the aqueous and organic phases respectively. A value of 132 cm^3/mole was chosen for V_c on the assumption that the density of liquid 8-quinolinol is 1·100 g/cm^3, slightly greater than that of quinoline (1·094 g/cm^3). The solubility parameter of the aqueous phase was taken as equal to 16·3. This value is substantially equal to the one obtained by Suzuki *et al.*[3] and gave values of K_D^x close to those obtained experimentally. It is substantially lower than the value 24·0 calculated from the heat of vaporization.[14] Since water is not a regular liquid, it cannot be expected to behave altogether normally. It can serve, however, as reference phase against which regular organic solvents may be compared.

According to the experimental results, the value of the solubility parameter of 8-quinolinol should be close to 10·5. A value of 10·6 was used to calculate the parabola represented by the solid line in Fig. 2. It will be noted that the experimental results for those solvents which should obey

the regular solution theory closely, such as n-hexane and carbon tetrachloride, lie on this line. All of the other solvents, with the exception of chloroform also lie close to the line.

The deviation observed in the case of chloroform may reflect significant solvent-solute interaction through hydrogen-bonding. The values for 1-bromobutane and bromochloromethane show some deviation. The rest of the solvents in the series studied show values close to a flat portion of the parabola covering about 2 units of solubility parameter.

Distribution of 8-quinolinol between nitroalkanes (and chloronitroalkanes) and aqueous buffer systems

In Fig. 3, the logarithm of the distribution ratios, D, of 8-quinolinol between water and mixtures of nitroalkanes and carbon tetrachloride are plotted against the logarithm of the solute concentration in the organic phase, at equilibrium. The distribution ratio between water and 1-nitroethane plus carbon tetrachloride varies markedly with solute concentration within the range explored (0·10–0·001 M). A less pronounced variation was observed with 1-nitropropane and 2-nitropropane. It was also observed that D in the 1-nitroethane–carbon tetrachloride–water system decreased when the proportion of nitroalkane increase (initial solute concentration about $10^{-2}M$). No marked dependence was observed when the proportion of nitropropanes in the mixture was changed. Figure 3 suggests the presence of a limiting value for D which seems to be reached at lower solute concentration for the nitropropanes than for nitroethane.

Although additional experimental studies are needed to postulate a quantitative explanation for the dependence, the results obtained point to a solvent-solute interaction as responsible for the

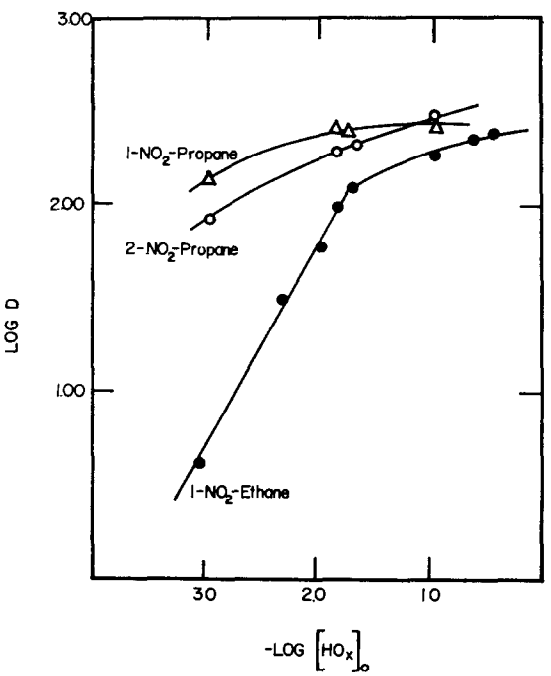

FIG. 3.—Distribution of 8-quinolinol between aqueous systems and 1:1 mole mixtures of carbon tetrachloride and some nitroalkanes at various values of $[HOx]_0$.

variation of D with solute concentration. The organic phase contains the nitroalkane and carbon tetrachloride; since carbon tetrachloride is a "non-polar" or "non-associated" liquid, it may be ruled out as interacting with the solute. The effect has to be ascribed solely to the nitroalkane.

To make a comparison between the behaviour of the nitro compound and those of the halogenated hydrocarbons, an equimolar mixture of it with carbon tetrachloride was used as the organic phase.

Its dielectric constant and solubility parameter were calculated as the sum of the contributions of each component with the help of:

$$\varepsilon_{mix} = \varepsilon_{NA} \cdot \phi_{NA} + \varepsilon_{CCl_4} \cdot \phi_{CCl_4}$$
$$\delta_{mix} = \delta_{NA} \cdot \phi_{NA} + \delta_{CCl_4} \cdot \phi_{CCl_4}$$

where ϕ is the volume fraction and the subscript NA refers to nitroalkanes.

The solubility parameter of the pure nitroalkanes was calculated from the heat of vaporization at 25°.

The values for D at an equilibrium ligand concentration in the organic phase of $10^{-2}M$ show an appreciable deviation from both plots in Figs. 1 and 2, in the case of 1-nitroethane. The values for the nitropropanes are closer to the plot but somewhat lower. 1-Nitropropane shows the higher D value. On the other hand, the values for D at an equilibrium ligand concentration in the organic phase of $10^{-1}M$ are surprisingly close to the dependence trend observed with the halogenated hydrocarbons, as can be seen in Figs. 1 and 2. On the basis of these observations 2-nitropropane gives slightly higher D values. Its deviation is in the same direction as that observed for chloroform. It may be noted that the active hydrogen is in a more symmetrical position in the case of 2-nitropropane than in either 1-nitroethane or 1-nitropropane. Also, 2-nitropropane, with a lower boiling point than 1-nitropropane, should be less associated. Moreover, the good correlation of D values with the dielectric constant and the solubility parameter, compared with the halogenated hydrocarbons, suggests that the extraction at D_{max} between water and nitroalkane–carbon tetrachloride systems would correspond to the extraction of molecular 8-quinolinol. It may be mentioned that the lower values of D for nitroethane are in qualitative agreement with its greater solubility in water. A few experiments with chloronitroalkanes were also performed. Because of their density, it was possible to use them as organic phases without dilution with carbon tetrachloride. They proved to be too reactive, however, and readily hydrolysed in contact with the aqueous phase. Nevertheless, it was possible, working quickly, to obtain distribution values with 1-chloro-1-nitropropane and 10^{-2} and $10^{-1}M$ 8-quinolinol solutions. The values of log D, 2·37 and 2·45 respectively, are surprisingly similar to the values for the simple nitroalkanes.

It must be concluded that, for 8-quinolinol and probably for its chelates as well, nitroalkanes offer no particular advantages as organic solvents over the halogenated hydrocarbons. Of this latter group, bromochloromethane seems to be about the best solvent, having a K_D value about 20% better than that of chloroform.

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Summary—The distribution constants of 8-quinolinol between water and a series of substituted aliphatic hydrocarbons, at 25°, are reported. The results are discussed in terms of dielectric constant and solubility parameter of the solvents. For 8-quinolinol, and possibly for its chelates, bromochloromethane, dibromomethane and chloroform seem to be about the best solvents, in that order. Among the solvents studied, chloroform shows significantly higher values than expected; the deviation may be explained as a specific interaction of the hydrogen-bonding type.

Zusammenfassung—Die Verteilungskonstanten von 8-Hydroxychinolin zwischen Wasser und einigen substituierten aliphatischen Kohlen-Wasserstoffen bei 25° werden mitgeteilt. Die Ergebnisse werden im Hinblick auf Dielektrizitätskonstante und Löslichkeitsparameter der Lösungsmittel diskutiert. Für 8-Hydroxychinolin und vielleicht auch für seine Chelate sind anscheinend Bromchlormethan, Dibrommethan und Chloroform in dieser Reihenfolge die besten Lösungsmittel. Unter den geprüften Lösungsmitteln zeigt Chloroform erheblich hohere Werte als erwartet; die Abweichung kann durch eine spezifische Wechselwirkung vom Wasserstoffbrückentyp erklärt werden.

Résumé—On donne les coefficients de partage de la 8-hydroxyquinoléine entre l'eau et une série d'hydrocarbures aliphatiques substitués, à 25°. On discute des résultats en fonction de la constante diélectrique et du paramètre de solubilité des solvants. Pour la 8-hydroxyquinoléine, et peut-être pour ses chélates, le bromochlorométhane, le dibromométhane et le chloroforme semblent être sensiblement les meilleurs solvants, dans cet ordre. Parmi les solvants étudiés, le chloroforme montre des valeurs notablement plus élevées que celles attendues; l'écart peut être expliqué par une interaction spécifique du type liaison hydrogéne.

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ANNOTATION

Explosion hazards with xenon trioxide solutions ("xenic acid")

THE strong oxidizing properties of aqueous xenon trioxide solutions ("xenic acid") have been recognized for some years.[1,2] That they are going to find wide application has become apparent with the recent publication of papers by Jaselskis and his co-workers.[3,4] These papers have stimulated interest amongst chemists who have not previously worked with xenon compounds. We have had several requests for solutions of xenon trioxide or for xenon fluorides for the preparation of such solutions, from people interested in carrying out work similar to that described in the papers cited. Generally, however, the people making the requests have been unaware of the dangers involved in the preparation and handling of such solutions, and attention should be drawn to these hazards.

Xenon trioxide solutions are prepared from either xenon tetrafluoride or xenon hexafluoride. The fluorides themselves are thermally stable, but their uncontrolled hydrolysis leads ultimately to the formation of solid, involatile xenon trioxide. This is extremely unstable and has an explosive force comparable to that of T.N.T. Few papers or reviews concerned with the preparation of xenon fluorides mention the dangers involved in their preparation and handling. A notable exception is the series of articles[5] in Inorganic Syntheses, which describes in detail some recommended methods for their preparation. Adequate detailed reference is made to precautions which should be taken when performing the syntheses.

There are warnings about the explosive nature of solid xenon trioxide in many of the papers concerned with it, (*e.g.*, references 6–9) and in recent review papers,[10–12] but only one of these[12] gives references to sources of information on hazards and safety precautions.

There are four main sources dealing with safety aspects: (1), a chapter of the book[13] edited by Hyman which followed the first Symposium on Noble Gas Chemistry in 1963; (2), an information sheet published by the Division of Operational Safety of the U.S.A.E.C.;[14] (3) a short article published in the Argonne National Laboratory Reviews;[15] and (4), two brief letters in the Journal of Chemical Education.[16] Of these (1) is readily available and is probably the most useful document on safety practices, (2) and (3) are not easily obtained (at any rate in Britain), and (4), though accessible, is not widely known amongst those concerned only with research. The best information available about the preparation of pure xenon trioxide *solutions* is in an excellent article by Appelman and Malm in Preparative Inorganic Reactions,[17] giving a recommended procedure by the hydrolysis of xenon hexafluoride. The hazards are clearly stated and points where special care is necessary are mentioned.

Because of the general lack or inaccessibility of safety information on noble gas chemistry, no excuse is made here for repeating recommendations which have been published elsewhere.

Precautions when handling fluorine

Fluorine is inherently dangerous because it is the most reactive element. It should therefore be treated with respect. Fluorine can be obtained either from electrolytic generators or from cylinders. Suppliers of fluorine publish data sheets which describe in detail precautions to be taken when handling fluorine.[18] No worker should attempt to use fluorine without first consulting these sheets. It is also desirable to consult experienced personnel.

Precautions when handling xenon compounds

All xenon compounds must be treated as potential sources of explosive solid xenon trioxide, because this is so readily formed by the hydrolysis of xenon tetrafluoride, xenon hexafluoride and xenon oxide tetrafluoride ($XeOF_4$). No exception should be made for xenon difluoride, which, although it does not form xenon trioxide on hydrolysis, is often contaminated with xenon tetrafluoride which does. Xenon fluorides and oxide fluorides, if contaminated with organic materials, should also be treated as sensitive explosives.

Safety glasses and/or a face-mask should be worn at all times when xenon compounds are being

prepared or manipulated. Leather gloves with cuffs, which give protection to the wrists, should be worn whenever xenon trioxide is handled, especially in equipment subject to fragmentation (*e.g.*, glass).

When xenon compounds are handled in vacuum systems it is inevitable that some materials will find their way into the traps protecting diffusion pumps. These materials often explode if the trap is allowed to warm up, or if moisture leaks into the system. Sometimes xenon compounds collected in glass traps react with the glass to produce explosive materials. Liquid-nitrogen dewars or traps of this kind should be surrounded with metal cylinders to direct the force of any explosion upwards. The traps should not be allowed to warm up whilst containing residues. They should be cleaned out frequently to avoid the collection of large quantities of explosive materials. The best way to clean the traps is to allow dilute alkali to be drawn into the evacuated trap at liquid-nitrogen temperature. The trap is then allowed to warm slowly to room temperature. The whole operation is particularly dangerous, there being a risk of a serious explosion at any time before thawing is complete. The preparation of xenon trioxide solutions by the addition of water to xenon tetrafluoride or hexafluoride is equally hazardous.[19] Appropriate precautions should be taken; face-masks, leather gloves and if possible protective canvas or PVC clothing should be worn. Substantial safety screens should be used.

All containers should be labelled with the nature of the contents. Where there is any chance that xenon trioxide is present the explosion hazard should be clearly indicated.

Precautions when handling xenon trioxide solutions

Xenon trioxide solutions are usually prepared from xenon hexafluoride by hydrolysis. This is a more efficient reaction than the hydrolysis of xenon tetrafluoride, but it is also more violent. Two different methods are possible. The first is the procedure recommended by Appelman and Malm.[19] This should be followed in every detail and extreme safety precautions should be taken (see previous section). The second method has been developed by Huston.[20,21] The method is probably safer than that of Appelman and Malm since, if properly executed, it avoids the sudden mixing of large quantities of xenon hexafluoride with water. The xenon hexafluoride is contained in a U-shaped Monel weighing-can fitted with two Hoke A431 valves (recently recatalogued as Hoke type 4171M2B). The contents of the can are swept through Kel-F (polytrifluorochloroethylene) tubing into water by means of a stream of dry nitrogen, (see Fig. 1). The Hoke valve is removed from one side of the U-tube, and the Kel-F tubing is connected directly to the exit of the can to minimize possible metallic contamination. The water is held in a Teflon (polytetrafluoroethylene) bottle in which the solution is afterwards stored. The hydrolysis reaction is carried out over a period of several hours.[20] It is most important that when this procedure is used a positive pressure of dry nitrogen *must* be maintained *at all times* when starting the hydrolysis.[21] If pressure is allowed to fall, back-suction of water into the weighing-can will cause explosions.

Once prepared, xenon trioxide solutions are safe provided they are not allowed to come to dryness. Containers, glass rods, pipettes *etc.*, wetted with xenon trioxide solution will deposit solid xenon trioxide if allowed to dry and explosions will result when they are handled. Ground-glass stoppered bottles should be avoided. These are not usually air-tight. Solid xenon trioxide may be formed in the

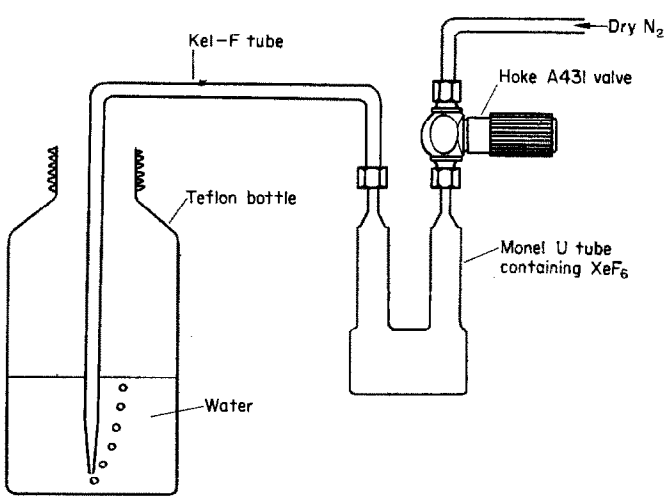

FIG. 1.—Apparatus for hydrolysis of xenon hexafluoride.[20,21]

neck of the bottle and in an extreme case the contents may evaporate slowly to dryness. Solutions are best stored in Teflon bottles with screw-tops or glass vessels with air-tight Teflon stoppers. Polythene appears to be subject to attack by xenon trioxide solutions, presumably by some kind of oxidation, and does not, therefore, make good containers.[22] Clean systematic working is essential. Scrap should not be allowed to collect.

This article is not intended to be fully comprehensive. Anyone intending to enter the field should at least consult the references cited here, many of which contain additional information. Better still, experienced personnel should be consulted.

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Summary—Attention is drawn to the explosion hazards associated with xenic acid (xenon trioxide solution) and hence all xenon compounds that can yield xenon trioxide by hydrolysis.

Zusammenfassung—Es wird auf die Explosionsgefahr von Xenonsäure (Xenontrioxidlösung) und allen Xenonverbindungen, die zu Xenontrioxid hydrolysieren können, aufmerksam gemacht.

Résumé—On attire l'attention sur les risques d'explosion associés à l'acide xénique (solution de trioxyde de xénon) et partant à tous les composés du xénon pouvant donner du trioxyde de xénon par hydrolyse.

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PRELIMINARY COMMUNICATIONS

Spectrophotometric determination of chromium with Xylenol Orange and Methylthymol Blue

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CHROMIUM(III) reacts with EDTA to form a purple complex. This reaction has been widely used for the photometric determination of chromium.[1-8] It has been found that other polyamino carboxylic acids also form purple complexes with chromium(III) upon heating, but these analogues do not offer any advantages over EDTA as a chromogenic reagent for chromium because of lack of sensitivity. It was thought that a phenolic dye containing an iminodiacetic acid group [—$N(CH_2COOH)_2$] or a carboxylic group might form an intensely coloured complex with chromium(III) upon heating. Xylenol Orange and Methylthymol Blue were chosen to test the speculation. The experimental results have confirmed the prediction. The chromium(III) Xylenol Orange complex is red with a maximum absorption at 530 mμ and the chromium(III) Methylthymol Blue complex is straw-yellow-red with a maximum absorption at 560 mμ. It seems that the substituted iminodiacetic acids are chromogenic reagents for chromium(III). This paper describes preliminary results for determination of chromium with Xylenol Orange and Methylthymol Blue.

EXPERIMENTAL

Reagents

Xylenol Orange solution, $1 \times 10^{-3}M$. Prepared from the sodium salt of 5,5′-bis{[bis(carboxymethyl)amino]methyl}-*o*-cresolsulphonphthalein.

Methylthymol Blue solution, $1 \times 10^{-3}M$. Prepared from the pentasodium salt of 3,3′-bis{[bis(carboxymethyl)amino]methyl}thymolsulphonphthalein. The solution was acidified with a small amount of acetic acid.

Acetate buffer solution, pH 3. Prepared by mixing $2M$ monochloroacetic acid and $1M$ sodium acetate to give a reading of pH 3 on a pH meter.

Preparation of calibration curves

Transfer 0, 1·0, 2·0, 3·0 and 4·0 ml of $2{\cdot}5 \times 10^{-4}M$ potassium chromium sulphate solution to a series of 50-ml pyrex test-tubes, add 0·5 ml of the acetate buffer solution, and dilute to approximately 8 ml. Add 4 ml of $1 \times 10^{-3}M$ Xylenol Orange solution or Methylthymol Blue solution. Place the tubes in boiling water for 20 min. Cool to room temperature, transfer to a 25-ml volumetric flask, dilute to volume, and mix. Measure the absorbance at 530 mμ for the Xylenol Orange complex, or at 560 mμ for the Methylthymol Blue complex, against a reagent blank.

DISCUSSION AND RESULTS

Chromium(VI) does not react with Xylenol Orange or Methylthymol Blue. It is easily reduced to chromium(III). The red chromium(III) Xylenol Orange complex has a maximum absorption at 530 mμ. When Methylthymol Blue is in large excess, its chromium(III) complex has a maximum absorption at 560 mμ, but when chromium is in excess, a blue or violet chromium Methylthymol Blue complex is formed.

Similarly to NTA and EDTA, Xylenol Orange and Methylthymol Blue react with chromium(III) extremely slowly at room temperature. When microgram amounts of chromium were taken, no reaction between chromium and Xylenol Orange or Methylthymol Blue could be detected at room temperature for several hours. The colour reactions were noticed when the temperature exceeded 70° and were complete at 100° in 15–20 min. Rao and coworkers[2] reported the catalytic action of bicarbonate ion on the formation of the chromium(III) EDTA complex and Irving and Tomlinson[8] described the electron exchange catalysis in the formation of chromium(III) EDTA complex by chromium(II) generated by metallic zinc. The present author found a similar catalytic action of carbon dioxide gas at pH 5 on the formation of the coloured chromium(III) EDTA complex.

However, no catalytic action of bicarbonate, carbon dioxide, or metallic zinc on the formation of chromium(III) Xylenol Orange complex or chromium(III) Methylthymol Blue complex was observed at pH 3 and room temperature.

The molar absorptivity of the chromium(III) EDTA complex has been reported as varying from 155 to 201 by different authors.[3] The molar absorptivity of the chromium(III) Xylenol Orange complex was found to be $19{\cdot}0 \times 10^3$ which is comparable with those of other Xylenol Orange complexes.[4,5] Based on Sandell's expression, the sensitivity of the Xylenol Orange method is 0·003 μg. cm^{-2} for 0·001 absorbance. Methylthymol Blue is a less sensitive reagent for chromium than Xylenol Orange. The molar absorptivity of chromium(III) Methylthymol Blue complex has a value of $11{\cdot}5 \times 10^3$ and its sensitivity is 0·005 μg. cm^2 for 0·001 absorbance. The phenolic donor group adjacent to the iminodiacetic acid donor groups is mainly responsible for the high molar absorptivity of the Xylenol Orange complexes. Obviously, the chelation resulting in the formation of multiple rings causes a bathochromic shift.

There are not many sensitive reagents for chromium. Most existing photometric methods for chromium are based on oxidation of a dye by chromate ion. The Xylenol Orange method is a rare, sensitive colour reaction occurring through complex formation with chromium(III). Like other Xylenol Orange complexes, the chromium(III) complex is stable for at least a few days. Beer's law is obeyed for the range $4\text{–}40 \times 10^{-6} M$ chromium for both the Xylenol Orange and Methylthymol Blue methods.

When we had finished the preliminary work, a brief note by Malát[6] was brought to our attention. It noted that Xylenol Orange gave a red colour with chromium(III) in a weakly acidic medium upon heating, and that the complex formed had a maximum absorption at 490 mμ and might be suitable for the colorimetric determination of chromium. No procedure was given. It is surprising to note the maximum absorption at 490 mμ reported by Malát because Xylenol Orange shows a maximum absorption at 440 mμ and most red Xylenol Orange complexes have their maximum absorptions around 535 mμ or at longer wavelengths.

Xylenol Orange is not a selective reagent, but it is possible to correct for the absorbance obtained at room temperature due to interfering metals if their amounts are smaller than the concentration of chromium to be determined. It should be noted that niobium, aluminium, palladium and chromium are the only four metals known to require a temperature of 100° to hasten their complex formation with Xylenol Orange and Methylthymol Blue.

Further investigation is being undertaken to determine many factors affecting the colour development, complex formation, and interferences when Xylenol Orange and Methylthymol Blue are used as chromogenic reagents for chromium.

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Summary—A new simple and sensitive method for determining traces of chromium is described. Xylenol Orange and chromium(III) form a red complex at pH 3 on heating in boiling water for 20 min. The molar absorptivity is $19{\cdot}0 \times 10^3$. No catalytic action of the bicarbonate ion, carbon dioxide, or chromium(II) generated by metallic zinc was observed. Methylthymol Blue is a less sensitive reagent for chromium, the molar absorptivity being $11{\cdot}5 \times 10^3$.

Zusammenfassung—Eine neue einfache und empfindliche Methode zur Bestimmung von Chromspuren wird beschrieben. Xylenolorange und Chrom(III) bilden bei pH 3 und 20-minütigem Erhitzen in siedendem Wasser einen roten Komplex. Der molare Extinktionskoeffizient ist $19{,}3 \cdot 10^3$. Eine Katalyse von Bicarbonat, Kohlendioxid oder durch metallisches Zink erzeugtem Chrom(II) wurde nicht beobachtet. Methylthymolblau ist als Reagens für Chrom weniger empfindlich, der molare Extinktionskoeffizient beträgt $11{,}5 \cdot 10^3$.

Résumé—On décrit une nouvelle méthode simple et sensible pour la détermination de traces de chrome. Le Xylénol Orangé et le chrome(III) forment un complexe rouge à pH 3 par chauffage dans l'eau bouillante pendant 20 mn. Le coefficient d'absorption moléculaire est 19,0 × 10^3. On n'a pas observé d'action catalytique de l'ion bicarbonate, du gaz carbonique ou du chrome(II) engendré par le zinc métallique. Le bleu de méthylthymol est un réactif moins sensible du chrome, le coefficient d'absorption moléculaire étant 11,5 × 10^3.

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Solvent extraction of ammine complexes

THE separation of metals based on their ability to form halide and thiocyanate complexes extractable by many oxygen-containing organic solvents is widely used in analytical chemistry.[1] Extractions based on the decrease in hydration produced by the formation of simple ammine complexes [$Me(NH_3)_n^{j+}$] have not been reported. It is obvious that the differences in the stabilities of ammine complexes of metals could be used for useful extraction separations. The ammine complexes should be extractable as ion-association species[2] if a highly polar solvent and large hydrophobic organic anions are used.

The results obtained in our laboratory are in accord with these ideas. If nitrobenzene is used as the solvent, and dipicrylaminate (DPA^-) or tetraphenylborate (TPB^-) as the anion, the ammine complexes of zinc and of cobalt can be extracted effectively. Typical results are summarized in Table I, from which it can be seen that both the formation of ammine complexes and the presence of large anions are necessary for the metal extraction. Consequently, it is believed that the species $Zn(NH_3)_n^{2+}$ and DPA^- (or TPB^-) exist in the organic phase and that partial association between them may occur.[3]

The driving force behind this type of extraction is the squeezing out of large, unhydrated, low-charged ions by the hydrogen-bonded water structure.[4] The effect is to force these ions together so as to maximize the water-water interactions and minimize the disturbance caused in the water structure by the presence of these ions, and the ion-pairs formed in this way are then easily extracted. The cations accompanying the anions in the organic phase are those with the largest crystallographic radius and the smallest degree of hydration. Consequently, the sequence of increasing extractability

TABLE I

$\log [NH_4^+]$	$\log [NH_3]$	$\log [DPA^-]_{org}$	$\log D_{Zn}$	$\log \frac{D_{Zn}}{D_{NH_4}}$	$\log \frac{D_{Zn}}{D_{Cs}}$	$\log \frac{D_{Zn}}{D_{Sr}}$	$\log \frac{D_{Zn}}{D_{Co}}$
−1·30	−2·17	−1·70	0.11	0·51	−1·49	1·93	0·91
−1·30	−1·67	−1.70	2·16	2·56	0·56	3·83	2·58
−1·30	−1·17	−1·70	2·51	2·91	0·91	~4·30	1·99
−1·30	−0·67	−1.70	2·49	2·88	0·88	~4·30	1·73
−1·30	−1·67	−3·0	−0·32	1·37	−0·63	—	—
−1·30	−1·67	−2·3	0·52	1·52	−0.48	—	—
—	−0·67	−1·70*	1·68	—	—	—	—

* $[NaTFB]_{org}$.

Résumé—On décrit une nouvelle méthode simple et sensible pour la détermination de traces de chrome. Le Xylénol Orangé et le chrome(III) forment un complexe rouge à pH 3 par chauffage dans l'eau bouillante pendant 20 mn. Le coefficient d'absorption moléculaire est 19,0 × 10^3. On n'a pas observé d'action catalytique de l'ion bicarbonate, du gaz carbonique ou du chrome(II) engendré par le zinc métallique. Le bleu de méthylthymol est un réactif moins sensible du chrome, le coefficient d'absorption moléculaire étant 11,5 × 10^3.

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−1·30	−1·67	−2·3	0·52	1·52	−0.48	—	—
—	−0·67	−1·70*	1·68	—	—	—	—

* $[NaTFB]_{org}$.

is $Ca^{2+} < Li^+ < Na^+ < NH_4^+ < K^+ < Rb^+ + < Cs^+ < NC_2H_5^+ < Zn(NH_3)_4^{2+}$. The possibility of a number of interesting cation separations is obvious.

A disadvantage of the extraction of ammine complexes in some cases results from the need to use a rather high pH in the aqueous phase, so causing precipitation of some metals unless they are present in tracer concentrations. This could be eliminated by suitable masking, but considerable changes in the selectivity of these extraction separations might then be produced. When ethylenediamine is used instead of ammonia, higher D_{Zn} values (distribution coefficients) are obtained. Further work is in progress.

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Summary—The ammine complexes of zinc and of cobalt(II) can be extracted effectively as the dipicrylaminates or tetraphenylborates by using nitrobenzene as the solvent.

Zusammenfassung—Die Amminkomplexe von Zink und Kobalt(II) können als Dipikrylaminate oder Tetraphenyloborate gut in Nitrobenzol extrahiert werden.

Résumé—On peut efficacement extraire les complexes ammino du zinc et du cobalt(II) à l'état de dipicrylaminates ou de tétraphénylborates en utilisant comme solvant le nitrobenzène.

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SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF GOLD BY RADIOACTIVE ISOTOPE-DILUTION ANALYSIS

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Summary—A radioactive isotope-dilution method for the determination of traces of gold has been developed. It is based on the solvent extraction of gold diethyldithiocarbamate from 0·5*N* sulphuric acid containing ascorbic acid, by means of a substoichiometric amount of zinc diethyldithiocarbamate in chloroform. The separation has been applied to the analysis of gold-doped semiconductor-grade silicon and of gold-bearing ores. Amounts of gold down to 5×10^{-7} g/20 ml of test solution can be determined.

THE success of a neutron-activation method for the substoichiometric determination of traces of gold[1] suggested that an isotope-dilution method involving the same separation procedure could be developed. Isotope-dilution analysis has been applied to the determination of a number of elements,[2] but no reference could be found to its application to gold.

EXPERIMENTAL

Apparatus

Scintillation counter. The detector used was a 1·75-in. diameter × 2 in. NaI(Tl) well-type crystal (well-volume 5 ml), associated with a single channel gamma-ray spectrometer. A discriminator voltage setting corresponding to 0·07 MeV ensured a high sensitivity of counting the ^{198}Au activity.

Reagents

All reagents were prepared from analytical reagent grade chemicals unless otherwise stated. Electronic grade nitric and hydrochloric acids and micro analytical reagent grade sulphuric acid were used.

Labelled gold stock solution (1·0 *μg/ml in* 2·5*M hydrochloric acid*). About 10 mg of metallic gold (metal leaves *ca.* 0·1-*μ* thick, General Chemical Co., Division of Fisons Scientific Apparatus Ltd., Loughborough, England) were irradiated in a flux of 6×10^{11} neutrons cm^{-2} sec^{-1} for 6 hr (Universities of Manchester and Liverpool Research Reactor). The amount of ^{198}Au produced by ^{197}Au(n, γ)^{198}Au($t_{1/2}$ = 2·7 days; σ = 96 barns; β^- = 0·96 MeV; γ = 0·41 MeV)[3] was sufficient for experiments over about 17 days. After irradiation the gold was dissolved in *aqua regia*, and the solution was twice evaporated almost to dryness with hydrochloric acid to remove oxides of nitrogen. The solution was then diluted appropriately with 2·5*M* hydrochloric acid.

Non-labelled gold stock solution (1·0 *μg/ml in* 2·5*M hydrochloric acid*). Prepared from a weighed amount of non-irradiated gold as described above.

Gold solutions of lower concentrations were prepared by dilution of the stock solutions.

Zinc diethyldithiocarbamate solution (1×10^{-4}*M*). Prepared by mixing 25 ml of zinc sulphate solution (0·0285 g of the heptahydrate) with 125 ml of an aqueous solution of sodium diethyldithiocarbamate [0·0225 g, preferably freshly purified (see p. 880)] containing 5 ml of 0·2*M* sodium acetate/acetic acid buffer (pH 4·7). The precipitate formed was extracted with two 200-ml portions of chloroform, and the combined extracts diluted to 500 ml with the same solvent. The reagent was standardised by a spectrophotometric extractive titration with 10^{-4}*M* copper solution (prepared by

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dilution of $10^{-2}M$ copper sulphate standardised iodometrically). The absorbance of the copper diethyldithiocarbamate was measured at 440 mμ (zinc diethyldithiocarbamate shows no absorbance at this wavelength).

Distilled water. The water used must be as pure as possible, and we have found that double distilled as obtained from a Scorah Type 4 glass distillation unit (L.V.D. Scorah, 44 Northfield Road, Birmingham 30, England) satisfactory. To check the purity a sample was extracted with dithizone ($5 \times 10^{-6}M$ in chloroform). No change in the green colour of the reagent was taken as the criterion of purity.

DEVELOPMENT OF METHOD

Preliminary experiments

Our neutron-activation studies[1] showed that 0·01–10N sulphuric or hydrochloric acid was a suitable medium from which to extract gold reproducibly with copper diethyldithiocarbamate in chloroform. Preliminary experiments showed that the following factors were of importance in the

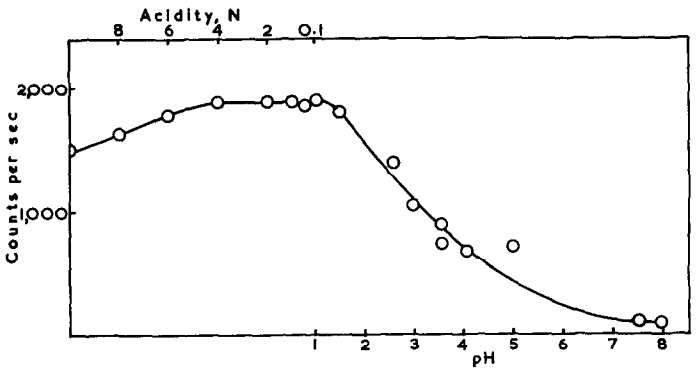

FIG. 1.—Influence of acidity on the substoichiometric extraction of gold from sulphuric acid with zinc diethyldithiocarbamate in chloroform.

extraction of gold under the conditions required for isotope-dilution analysis.

1. Sulphuric acid is a better solvent medium than hydrochloric acid—chloride competes more strongly with chelating agent for the gold in the absence of a gold-carrier.
2. Zinc diethyldithiocarbamate gives better extraction of gold than does copper diethyldithiocarbamate—the difference in extraction constants is greater for zinc and gold than for copper and gold.
3. The presence of a mild reducing agent, ascorbic acid, is particularly advantageous—reduction of gold to gold(I) seems necessary for complete complex formation.

Reproducibility

The optimum conditions for a reproducible substoichiometric extraction of gold diethyldithiocarbamate in the presence of ascorbic acid were next established.

Any sulphuric acid concentration from 0·1 to 4N was found to be suitable (Fig. 1). For all further experiments 0·5N sulphuric acid (containing 1 ml of 1% ascorbic acid solution) was used. Extraction equilibrium was reached in 1·5 min with 1·25 μg of gold and in 2 min with 0·1 μg (Fig. 2). An extraction time of 5 min was therefore used in all further experiments.

Stability of solutions. The reproducibility of the substoichiometric separation using a labelled gold solution of 1·0 μg/ml was good (Fig. 3, upper curve), but when the gold concentration was 0·1 μg/ml the reproducibility became poor. This was traced to two causes: the labelled gold solution in 1M hydrochloric acid was slowly hydrolysing, and the zinc diethyldithiocarbamate solution in chloroform ($5 \times 10^{-8}M$) was not very stable.

The maximum period during which different solutions of gold and zinc diethyldithiocarbamate were found to be stable (not more than 10% change from the initial concentration) is given in Table I. If the sodium diethyldithiocarbamate was purified to remove oxidation products,[4] the zinc diethyldithiocarbamate solution prepared from it was more stable ($2·5 \times 10^{-7}M$ solution stable for at least 3 hr).

With a freshly labelled gold solution (0·1 μg/ml) and fresh reagent solution ($5 \times 10^{-8}M$) good reproducibility of separation was now achieved (Fig. 3, lower curve), but below this concentration reproducibility was poor.

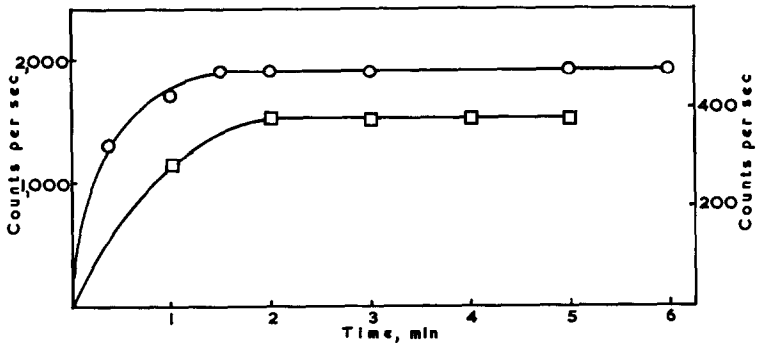

FIG. 2.—Time necessary to reach extraction equilibrium in the substoichiometric extraction of gold with zinc diethyldithiocarbamate in chloroform (20 ml of 0·5*N* sulphuric acid).
○—Left-hand axis, 1·25 μg of gold;
□—Right-hand axis, 0·10 μg of gold.

TABLE I.—STABILITY OF GOLD AND ZINC DIETHYLDITHIOCARBAMATE SOLUTIONS

Solution	Concentration		Maximum period of stability, *hr*
	μg/ml	*M*	
Gold in 2·5*M* hydrochloric acid	5·40		504 (21 days)
	1·06		53
	0·12		24
Zinc diethyldithiocarbamate in chloroform		1×10^{-6}	4
		1×10^{-7}	1·5
		5×10^{-8}	0·5
		1×10^{-8}	0·25

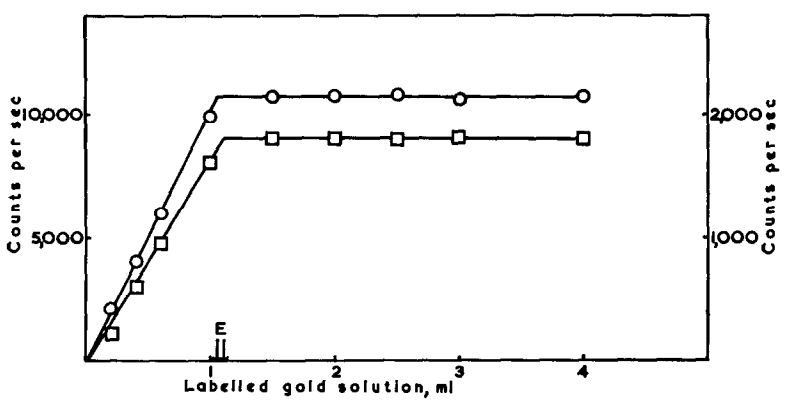

FIG. 3.—Reproducibility of the substoichiometric extraction of gold with zinc diethyldithiocarbamate in chloroform (20 ml of 0·5*N* sulphuric acid; 3 ml of organic phase separated for counting; *E* denotes the equivalence point).
○—Left-hand axis, extraction of labelled gold solution (1·0 μg/ml) with 5 ml of $5 \times 10^{-7}M$ zinc diethyldithiocarbamate;
□—Right-hand axis, extraction of labelled gold solution (0·1 μg/ml) with 5 ml of $5 \times 10^{-8}M$ zinc diethyldithiocarbamate.

Role of chloride ions

Very dilute gold solutions are known to undergo hydrolysis especially if the temperature is increased. Chloride ions in sufficient quantity retard hydrolysis, but they can also compete with the chelating agent for the gold, thus preventing complete consumption of the substoichiometric amount of chelating agent. Therefore the concentration of chloride in the test solution is very critical, and that permissible will depend on the gold concentration; it is given in Table II. It is advisable to prepare the labelled gold solutions in 2·5*M* hydrochloric acid. If the amount of chloride ions introduced into a test solution by the addition of the labelled gold is more than can be tolerated (Table II), it is best to make a more concentrated labelled gold stock solution and to dilute it with water to the desired concentration before use.

TABLE II.—MAXIMUM CONCENTRATION OF CHLORIDE IONS THAT CAN BE TOLERATED FOR A GIVEN GOLD CONCENTRATION

Weight of gold in 20 ml of test solution, μg	Maximum concentration of chloride ions, M
1·0	0·36
0·5	0·18
0·2	0·06
0·1	0·05

Accuracy and precision

To a series of 50-ml separatory-funnels 20 ml of 0·5*N* sulphuric acid were added followed by 1·0 ml of labelled gold solution (1·06 μg/ml) and 1·0 ml of non-labelled gold solution (1·00 μg/ml). Then 1 ml of 1 % ascorbic acid solution was added followed by 5 ml of $5 \times 10^{-7}M$ zinc diethyldithiocarbamate in chloroform (substoichiometric amount). The funnels were shaken for 5 min, and 3·0 ml of the organic phase were separated for counting (activity A_2). An extraction was next made under the same conditions but with 2·0 ml of labelled gold solution and no non-labelled gold. The activity (A_1) of an equal volume of the organic phase was measured; this was sometimes referred to as the standard. The same procedure was used with labelled gold solutions of 0·1, 0·05, and 0·02 μg/ml concentration, the concentration of the chelating reagent being reduced accordingly.

The weight of non-labelled gold determined (x) can be calculated from the substoichiometric formula applied to isotope dilution[14]

$$x = y\left(\frac{A_1}{A_2} - 1\right)$$

where y = the weight of labelled gold used. A summary of our results is given in Table III.

TABLE III.—ACCURACY AND PRECISION OF SUBSTOICHIOMETRIC DETERMINATION OF GOLD BY ISOTOPE-DILUTION ANALYSIS

Weight (x) of non-labelled gold added, μg	Weight (y) of labelled gold added, μg	Weight ($\bar{x}$)* of non-labelled gold found, μg	Standard deviation, s†	Number of tests, n
1·00	1·06	1·03	0·057	15
0·10	0·11	0·10	0·016	15
0·05	0·05	0·06	0·013	10
0·01	0·02	0·01	0·003	6

* $\bar{x}$ = mean weight of non-labelled gold found.

† $s = \sqrt{\Sigma\Delta^2/n - 1}$, where Δ is the deviation from the mean.

Selectivity

The selectivity of the substoichiometric separation was investigated in the presence of a number of ions which either have extraction constants similar to that for the gold-diethyldithiocarbamate system,[5] or cause interference by some other mechanism, *e.g.*, reduction of the gold or oxidation of the diethyldithiocarbamate. The effect of reagents likely to be present after the dissolution of various test samples was also studied.

The procedure was that described under *Accuracy and precision* except that 1 ml of labelled gold solution (1·00 μg/ml in 2·5*M* hydrochloric acid) was used together with 100 or 1000 μg of the foreign ion to be examined. No non-labelled gold was added and the extraction was carried out with 4 ml of $2{\cdot}5 \times 10^{-7}M$ chelating agent, the activity of 2·5 ml of the organic phase being measured. Ideally, a result of $x = 0$ should be obtained because no non-labelled gold was present. In practice, if $-0{\cdot}1 > x > +0{\cdot}1$ μg the foreign ion was considered to interfere. The results of the selectivity studies are summarised in Table IV.

TABLE IV.—INFLUENCE OF FOREIGN IONS ON THE SUBSTOICHIOMETRIC EXTRACTION OF GOLD WITH ZINC DIETHYLDITHIOCARBAMATE

Foreign ion present		Foreign ion interfering	
1000 μg	100 μg	1000 μg	100 μg
Ag(I) As(III) As(V) Bi(III) Cd(II) Co(II) Cr(VI) Cu(II) Fe(II) Fe(III) Hg(II) In(III) Mo(VI) Ni(II) Pb(II) Pd(II) Pt(IV) Se(IV) Sb(III) Sb(V) Sn(II) Sn(IV) Te(IV) Tl(I) Zn(II)	Ag(I) Bi(III) Cr(VI) Cu(II) Hg(II) Pb(II) Pt(IV) Se(IV) Sb(III) Sn(II) Te(IV)	Ag(I)† Bi(III)† Cr(VI)† Cu(II)† Hg(II) Pd(II)§ Pt(IV) Se(IV) Sb(III) Sn(II)† Te(IV)	Ag(I)† Cu(II)‡ Hg(II)‡ Pd(II)§ Se(IV) Sb(III) Sn(II)† Te(IV)
6, 8 and 10*M* HNO_3 2*M* HBr 1 ml of 0·1*M* EDTA 1 ml of 1% DMG* 1 ml of 40% HF		2 ml of 10*M* HNO_3 1 ml of 2*M* HBr Cl^- (see Table II)	

* DMG = Dimethylglyoxime.
† Interference removed by preliminary extraction of gold with diethyl ether.
‡ Interference prevented by addition of EDTA.
§ Interference removed by extraction with dimethylglyoxime in chloroform.

Elimination of interferences

Three methods were investigated for eliminating interferences.

Preliminary extraction of gold. Extraction of gold into diethyl ether from chloride or bromide solutions is well known.[6–8] Some authors prefer the use of isopropyl ether[7] or ethyl acetate.[8] According to Morrison and Freiser[6] gold can be quantitatively extracted as $HAuCl_4$ into diethyl ether from 1·5–3*M* hydrochloric acid.

We found that when 1·0 μg of gold in 10 ml of 2*M* hydrochloric acid was shaken with 20 ml of diethyl ether for 3 min, about 80% of it was extracted. The interferences were studied by repeating this extraction in the presence of 100 or 1000 μg of the foreign ions concerned. The ether phase was separated and washed with 5 ml of 2*M* hydrochloric acid, added to 0·5 ml of 3*M* hydrochloric acid and heated at 50° on a water-bath to remove the ether. The resulting solution was diluted to 20 ml with 0·5*N* sulphuric acid and the gold separated and determined as under *Accuracy and precision*. Our results are summarised in Table IV.

If the hydrochloric acid concentration during evaporation of the diethyl ether was less than 3*M* hydrolysis occurred and not all the gold was in a form extractable by the chelating agent. Hydrolysis also occurred if sulphuric or nitric acid was used, even if they were more concentrated than 3*N*. During evaporation of the ether, gold was lost if chloride was absent. Therefore, chloride must be present to prevent hydrolysis and the loss during evaporation. The lowest amount of gold for which 0·5 ml of 3*M* hydrochloric acid would not interfere in the final separation was 0·5 μg (Table II).

The possibility of stripping the gold from diethyl ether solutions was studied; from an ether solution (20 ml) containing 0·7–0·8 μg of gold, half the gold could be transferred with two 20-ml portions of water, each shaken for 3 min with the ether phase. Before the substoichiometric separation it was then necessary to scrub with chloroform to remove traces of diethyl ether and to make the solution 0·5*N* with respect to sulphuric acid; if the ether was not removed it diluted the chelating agent, leading to erroneous results.

This stripping method was successful for solutions initially containing 1 μg of gold in 10 ml of 2*M* hydrochloric acid, the final concentration of gold being 0·4 μg/20 ml of solution which is near the lower limit for the method (0·1 μg/20 ml). The evaporation procedure gave about 0·8 μg of gold in 20 ml of test solution and therefore was preferred.

The extraction of gold from bromide solutions was then examined. Gold was more efficiently extracted by diethyl ether (*ca.* 80%) than by isopropyl ether (*ca.* 70%) with the same volumes and extraction times. The degree of stripping by water was higher from isopropyl ether solutions (*ca.* 85%) than diethyl ether solutions (*ca.* 70%). Even so, neither the evaporation nor the stripping method was successful, because traces of bromide seriously interfered in the final substoichiometric separation.

EDTA. Prevention of the interference of copper(II), bismuth(III), and mercury(II) by addition of 1 ml of 0·1*M* EDTA to the test solution before the substoichiometric separation (20 ml of 0·5*N* sulphuric acid; no ascorbic acid present) was studied. In 0·5*N* sulphuric acid there was no effect but in 0·1*N* sulphuric acid these interferences were overcome (Table IV), which can be explained from the conditional formation constants of their EDTA complexes.[10] The sulphuric acid must not be less than 0·1*N*, the lowest value suitable for the substoichiometric separation (Fig. 1).

Dimethylglyoxime. Many authors[11–18] have separated palladium from aqueous solutions of gold by extracting its dimethylglyoximate into chloroform. When 3 ml of 1% aqueous sodium dimethylglyoximate solution were added to the test solution before the substoichiometric separation (20 ml of 0·5*N* sulphuric acid; no ascorbic acid present) and the solution was let stand for 30 min, interference from palladium was eliminated by extracting the palladium complex with three 10-ml portions of chloroform, shaking the mixture for 3 min each time (Table IV).

ANALYSIS OF TEST SAMPLES

Because the concentration of chloride ions must be kept to a minimum, attempts were made to dissolve a gold-doped semiconductor-grade silicon sample in a mixture of nitric and hydrofluoric acids. Complete dissolution was achieved but a considerable loss of gold was incurred (*ca.* 50%). It was therefore necessary to include chloride ions, and after dissolution to reduce their concentration to a tolerable level by a diethyl ether extraction as used for the elimination of interfering species.

Procedure

To the test sample in a 50-ml Teflon beaker was added a weight (y) of labelled gold approximately equal to the weight of gold expected in the sample. The test sample was then dissolved, initially at room temperature and finally with gentle heating, in a mixture of nitric acid (10 ml) and hydrochloric acid (2 ml) with gradual addition of hydrofluoric acid (10 ml). The solution was then evaporated to about 0·5 ml and the evaporation repeated twice, each time after addition of 5 ml of hydrochloric acid. The resulting solution was diluted with water and 2*M* hydrochloric acid to give finally 10 ml of 2*M* hydrochloric acid solution. The activity of this solution was measured before extraction so that the recovery after the dissolution could be checked: it was at least 95% for each sample analysed.

The test solution, prepared as described above, was transferred to a 100-ml separatory funnel and shaken with 20 ml of diethyl ether for 3 min. The ether phase was scrubbed with 5 ml of 2*M* hydrochloric acid and transferred to a 50-ml beaker; then 0·5 ml of 3*M* hydrochloric acid was added and the solution heated at 50° on a water-bath to remove the ether. The resulting solution was transferred to a 100-ml separatory funnel and diluted to 20 ml with 0·5*N* sulphuric acid. If necessary, EDTA was added and palladium removed with dimethylglyoxime at this stage. Finally, 1 ml of 1% ascorbic acid solution was added and the gold extracted by a substoichiometric amount of zinc diethyldithiocarbamate solution in chloroform (4 ml of $2{\cdot}5 \times 10^{-7}M$ for gold-bearing ores; 4 ml of $5 \times 10^{-8}M$ for gold-doped semiconductor-grade silicon). The extractions were carried out for 5 min, then an aliquot of the organic phase (3·0 ml in each case) was removed for counting (A_2).

For the standard (run simultaneously) the same weight (y) of labelled gold was taken as that added to the sample, and it was extracted under the same conditions as for the test sample, and the same volume of organic phase was separated for counting (A_1). The weight of gold in the test sample (x) was then calculated, using the substoichiometric equation given above. The results of our analyses are given in Table V.

CONCLUSION

The method is capable of determining gold down to 0·1 μg/20 ml of test solution, but the need to have chloride ions present during dissolution of samples and also to prevent hydrolysis raises the lower limit to 0·5 μg/20 ml of test solution. The smallest amount of gold we have actually determined in a test sample by isotope dilution is $1{\cdot}45 \times 10^{-7}$ g, compared with 2×10^{-10} g by our neutron-activation method.[1] The limit of detection for gold is about three orders of magnitude lower by neutron activation, which is to be expected.

TABLE V—RESULTS OF ANALYSIS OF TEST SAMPLES

Sample*	Gold-bearing ore RSM 25†				
Weight, *g*	1·0061	0·9857	0·9830	0·9941	0·9872
Gold standard, *μg*	1·07	1·07	1·07	1·07	1·07
Activity from gold standard, *counts/sec*	255	255	255	637	637
Activity from sample, *counts/sec*	71	68	63	147	184
Gold found, *ppm*	2·78	3·00	3·32	3·58	2·66
Mean value, *ppm*			$3·0_7$		
Result of other authors, *ppm*			3·7‡		
Sample*	Gold-bearing ore RSM 349†				
Weight, *g*	1·0073	1·0133	0·9798	0·9760	0·9908
Gold standard, *μg*	1·07	1·07	1·07	1·07	1·07
Activity from gold standard, *counts/sec*	1098	1098	1098	637	637
Activity from sample, *counts/sec*	204	193	231	125	107
Gold found, *ppm*	4·70	4·98	4·10	4·48	5·36
Mean value, *ppm*			$4·7_8$		
Result of other authors, *ppm*			3·7‡		
Sample*	Gold-doped semiconductor-grade silicon 1153§				
Weight, *g*	1·2787		1·2196		1·8894
Gold standard, *μg*	0·49		0·49		0·49
Activity from gold standard, *counts/sec*	206		206		206
Activity from sample, *counts/sec*	159		158		154
Gold found, *ppm*	0·11		0·12		0·09
Mean value, *ppm*			0·11		
Result of other authors, *ppm*			$0·09_5$¶		

* All samples were counted for a period sufficient to yield a total of at least 10,000 counts; activity from gold standard is the mean of at least 3 results.

† Provided by Royal School of Mines, Imperial College, London, England.

‡ By fire assay at Royal School of Mines, using a factor-weight sample of 32·67 g.

§ Provided by Mullard Southampton Works, Southampton, England.

¶ See reference 1.

Antimony(III), selenium(IV), and tellurium(IV) interfered if present in amounts 100 times that of the gold (w/w), and mercury(II) and platinum(IV) if present in amounts 1000 times that of the gold (Table IV).

The results obtained from the analysis of the gold-doped semiconductor-grade silicon sample (Table V) were in good agreement with those previously found by neutron activation.[1] Those for the gold-bearing ores compared reasonably well with the values from fire assay, considering the large difference in the weights of sample taken for the two methods. Sample RSM 25 contains *ca.* 12 ppm of silver and RSM 349 *ca.* 11 ppm of silver, interference from which is eliminated during the extraction with diethyl ether. No interfering elements were known to be present in the semiconductor silicon sample.

If amounts of gold greater than about 10^{-6} g are to be determined, the use of radioisotopes generally offers no advantages over spectrophotometric methods. Our investigations[9] into a spectrophotometric titration procedure for gold, based on solvent extraction of its diethyldithiocarbamate into chloroform, indicated it had no advantage over existing spectrophotometric methods for this element.

Work is now in progress to establish the composition of the gold complexes extracted with diethyldithiocarbamic acid and dithizone under the various conditions that have been used in development of our neutron-activation and isotope-dilution methods for gold.

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Zusammenfassung—Eine Methode der Verdünnung mit einem radioaktiven Isotop zur Bestimmung von Goldspuren wurde entwickelt. Es beruht auf der Extraktion von Golddiäthyldithiocarbamat aus Ascorbinsäure enthaltender 0,5 M Schwefelsäure mit einer unterstöchiometrischen Menge Zinkdiäthyldithiocarbamat in Chloroform. Die Abtrennung wurde auf die Analyse von Gold-dopiertem Halbleitersilicium und von goldführenden Erzen angewandt. Goldmengen bis herunter zu $5 \cdot 10^{-7}$ g/20 ml Probelösung können bestimmt werden.

Résumé—On a élaboré une méthode radioactive par dilution isotopique pour le dosage de traces d'or. Elle est basée sur l'extraction par solvent du diéthyldithiocarbamate d'or à partir d'acide sulfurique 0,5 *N* contenant de l'acide ascorbique, au moyen d'une quantité substoechiométrique de diéthyldithiocarbamate de zinc en chloroforme. On a appliqué la séparation à l'analyse du silicium qualité semiconducteur dopé à l'or et à celle de minerias aurifères. On peut doser des quantités d'or aussi faibles que 5×10^{-7} g/20 ml de solution essai.

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ÉTUDE DE LA FORMATION DES DODECATUNGSTATES ET LE DOSAGE DES ISO- ET HÉTÉRODODECA-TUNGSTATES A L'AIDE DU CHLORURE DE TETRAPHÉNYLPHOSPHONIUM

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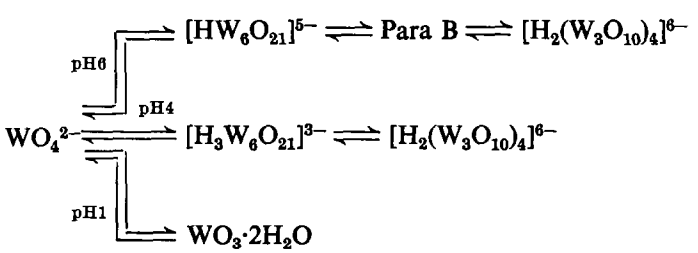
Résumé—Dans le présent travail en expose une étude physico-chimique sur les conditions de formation (pH, température, temps) et de séparation de dodécatungstates à l'aide du chlorure de tétraphénylphosphonium. Dans la série des iso- et hétéropolytungstates, seuls les anions de forme $[XW_{12}O_{40}]^{(8-n)-}$ (où n dénote l'état d'oxydation de l'atome X) précipitent avec ce réactif.

La réaction est quantitative et à l'aide de ce réactif on a réussi à séparer le dodécatungstate sous forme de précipité d'un mélange d'anions tungstiques.

En utilisant $[(C_6H_5)_4P]Cl$ comme réactif spécifique pour l'anion dodécatungstique, dans l'étude de la condensation de Na_2WO_4 sous l'action des acides forts, on a établi que cette forme 12 condensée de Na_2WO_4 commence à apparaître à pH $\sim$ 6, tandis qu'à pH $\sim$ 2 tout le tungstate présent est transformé en dodécatungstate. Les facteurs tels que la dilution, le temps et la température dans cet intervalle de pH 2–6 influencent le processus de condensation dans le sens de la formation de l'anion dodécatungstique. La réaction mentionnée est utilisée pour le dosage d'une série de 12-tungstates.

L'ÉTUDE complexe des espèces d'anions tungstiques en solution, constitue un chapitre très discuté de la littérature specialiseé. Parmi les méthodes utilisées, nous mentionnons: les méthodes conductimétriques,[1–3] potentiométriques,[4–6] de diffusion,[7,8] de dialyse,[6,8] polarographiques,[7,9–11] chromatographiques,[3,12,13] réfractométrique,[14] d'ultracentrifugation et mesures de densités,[15] radiochimiques,[16,17] de spectres Raman,[18] spectres d'absorption,[19] spectres IR,,[20] *etc.*

Nous donnons ci-dessous l'un des schémas, qui contient les espèces d'anions tungstiques probablement formés au cours de l'acidification d'une solution de Na_2WO_4 avec des acides forts.[21]



(I)

Dans le système complexe (I) il est difficile d'identifier chimiquement chaque espèce ou l'une d'entre elles par les réactifs connus et de suivre la formation du

dodécatungstate, étant donné que ces réactifs sont communs à plusieures des espèces formées.

Dans le présent travail, on apporte des nouvelles données à ce problème, par l'utilisation du chlorure de tétraphénylphosphonium comme réactif de precipitation. On a constaté que les espèces d'ions polytungstiques, tels que $[HW_6O_{21}]^{5-}$, $[NiW_6O_{21}]^{4-}$, $[CeW_8O_{28}]^{4-}$, $[ThW_8O_{28}]^{4-}$ et $[Co_2W_{12}O_{42}]^{8-}$ ne précipitent pas avec $[(C_6H_5)_4P]Cl$. Seuls ceux de forme dodécatungstique $[XW_{12}O_{40}]^{(8-n)-}$ tels que $[H_2W_{12}O_{40}]^{6-}$, $[SiW_{12}O_{40}]^{4-}$, $[PW_{12}O_{40}]^{3-}$, $[BW_{12}O_{40}]^{5-}$ et $[CoW_{12}O_{40}]^{5-}$ forment des sels de tétraphénylphosphonium, difficilement solubles dans l'eau, cristallins et stables (Tableau I).

TABLEAU I.—RÉSULTATS DES ANALYSES DE DODÉCA- ET HÉTÉRODODÉCATUNGSTATES

Combination	WO_3		C		P		H		$SiO_2 + WO_3$	
	calc. %	trouvé %	calc. %	trouvé %	calc. %	trouvé %	calc. %	trouvé %	calc. %	trouvé %
$[(C_6H_5)_4P]_6[H_2W_{12}O_{40}]$	57,0	56,6	35,4	33,8	3,8	3,1	2,6	2,5	—	—
$[(C_6H_5)_4P]_4[SiW_{12}O_{40}]$	—	—	27,2	26,5	2,9	2,5	1,9	2,0	67,3	65,9
$[(C_6H_5P]_3[PW_{12}O_{40}]$	70,1	70,8	22,0	21,9	3,1	2,9	1,8	2,0	—	—
$[(C_6H_5)_4P]_5[BW_{12}O_{40}]$	58,8	58,4	30,4	29,5	3,8	3,9	2,1	1,9	—	—

La précipitation du dodécatungstate de tétraphénylphosphonium a lieu probablement selon la réaction suivante:

$$[XW_{12}O_{40}]^{(8-n)-} + {}^{8-n}[(C_6H_5)_4P]^+ = [(C_6H_5)_4P]_{8-n}[XW_{12}O_{40}]$$

où n dénote l'état d'oxydation de l'atome X.

Nous avons suivi par potentiométrie, sous l'action d'ions H^+, la condensation de Na_2WO_4 en absence et en présence du chlorure de tetraphénylphosphonium. Les valeurs du pH obtenues dans les deux titrages potentiométriques s'inscrivent sur la même courbe (Fig. 1). Elle montre d'une part que la variation du pH n'est pas influencée par la présence du chlorure de tétraphénylphosphonium et d'autre part dans la solution qui contient le réactif on observe l'apparition d'un précipité à partir de pH $\sim$ 6. Ceci montre l'apparition d'ions dodécatungstiques, qui s'intensifie si l'on continue d'ajouter de l'acide chlorhydrique.

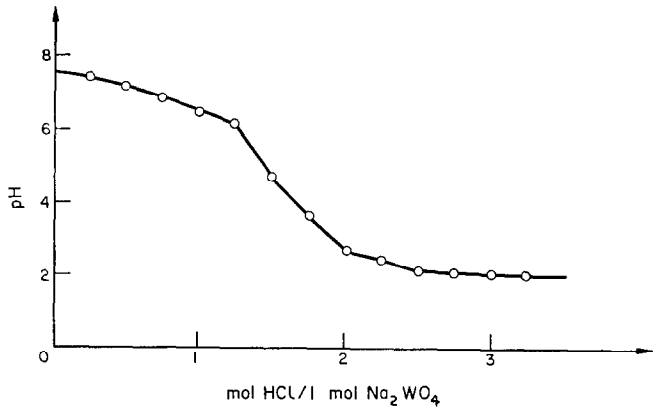


FIG. 1.—Le courbe potentiométrique des systemes (Na_2WO_4 + HCl) et (Na_2WO_4 + $[(C_6H_5)_4P]Cl$ + HCl).

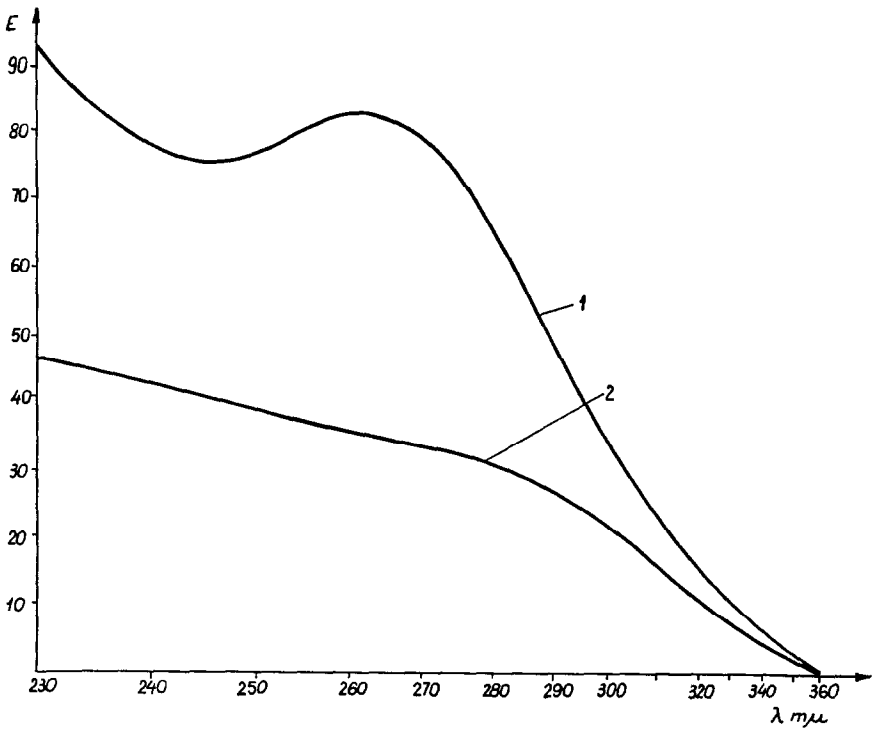


FIG. 2.—Spectre d'absorbtion de deux fractions de tungstates obtenues par la chromatographie d'une solution de Na_2WO_4 à pH = 4,5.
1. La fraction qui reste au point de dépôt.
2. La fraction qui va de front avec le solvent.

Par des séparations chromatographiques sur papier en solution saturée de NaCl et des déterminations du spectre d'absorption UV sur les solutions aqueuses de Na_2WO_4, pH 2–6, on a constaté que seule la fraction qui reste au point de dépôt et qui présente un maximum d'absorption à 257 mμ (Fig. 2) (spécifique pour l'anion métatungstique[19]) précipite avec $[(C_6H_5)_4P]Cl$.

D'autre part, l'analyse des précipités obtenus des mélanges de 0,01*N* Na_2WO_4 et $[(C_6H_5)_4]Cl$ portés à pH 6,00; 4,30; 2,80; 2,00; 1,50; conduit toujours à une seule combinaison: $[(C_6H_5)_4P]_6[H_2W_{12}O_{40}]$.

Les mêmes essais (Tableau II) montrent encore que le poids de précipité augmente à mesure que le pH décroît et que pour pH $\sim$ 2 tout le tungstène se trouve dans le précipité. À pH $\sim$ 1 le $WO_3 \cdot 2H_2O$ en solution commence a précipiter.

TABLEAU II.—LA PRÉCIPITATION DU MÉLANGE DE 0,01*M* Na_2WO_4 + $[(C_6H_5)_4P]Cl$ PORTÉ A DIVERS pH

pH	W en solution, *g*	W précipité, *g*	W précipité, %
7,00	0,09200	—	—
6,00	0,09200	0,00602	6,6
4,30	0,09200	0,04610	50,1
2,80	0,09200	0,08272	89,9
2	0,09200	0,09208	100,1
1,5	0,09200	0,09132	99,3
1	commence a précipité $WO_3 \cdot 2H_2O$		

De plus l'influence du temps et de la température sur le processus de condensation de Na_2WO_4 a été étudiée sur deux séries d'essais; l'une à pH = 5,5 et l'autre à pH = 3,5. La précipitation des deux séries de solutions avec $[(C_6H_5)_4P]Cl$ a été effectuée immédiatement, 24 h ou 48 h après l'acidification des solutions aux températures de 20° et 100°. Après filtration des précipités, le pH de chaque solution a été mesuré.

Les résultats mentionnés au Tableau III montrent que: la précipitation est plus riche dans les solutions de la série ayant un pH plus bas; le poids du précipité formé croît avec le temps; le pH des solutions, après filtration des précipités, croît avec le temps; la température accélère beaucoup le processus de condensation de Na_2WO_4 et la précipitation est plus abondante dans les solutions bouilles.

TABLEAU III.—CONDENSATION DES SOLUTIONS DE 0,01*M* Na_2WO_4 SOUS L'ACTION DE 0,1*M* HCl EN FONCTION DE pH, DU TEMPS ET DE LA TEMPÉRATURE

pH initial	5,5	5,5	5,5	3,5	3,5	3,5	5,5	3,5
Temps, *h*	0	24	48	0	24	40	1/6	1/6
Température, °*C*	20	20	20	20	20	20	100	100
W précipité, %	22,5	23,5	37,5	91,2	93,8	94,2	43,2	98,0
pH après la précipitation	5,6	5,6	5,7	3,6	4,5	4,7	5,7	5

La réaction entre $[XW_{12}O_{40}]^{(8-n)-}$ et $[(C_6H_5)_4P]^+$ étant quantitative, elle est utilisée pour le dosage des dodécatungstates. Dans la note présente on rapporte les résultats des dosages du métatungstate $[H_2W_{12}O_{40}]^{6-}$, du silicotungstate $[SiW_{12}O_{40}]^{4-}$, du phosphotungstate $[PW_{12}O_{40}]^{3-}$ et du borotungstate $[BW_{12}O_{40}]^{5-}$ (Tableau IV).

TABLEAU IV.—DOSAGE DE SOLUTIONS 0,01*M* DE DODÉCA- ET HÉTÉRODODÉCATUNGSTATES

Solution dosée	précipité obtenu	W	
		en solution, *g*	en précipité, *g*
$H_6[H_2W_{12}O_{40}]$	$[(C_6H_5)_4P]_6[H_2W_{12}O_{40}]$	0,03316	0,03308 ± 0,00008
$H_4[SiW_{12}O_{10}]$	$[(C_6H_5)_4P]_4[SiW_{12}O_{40}]$	0,04050	0,04055 ± 0,00002
$H_3[PW_{12}O_{40}]$	$[(C_6H_5)_4P]_3[PW_{12}O_{40}]$	0,03560	0,03558 ± 0,00009
$H_5[BW_{12}O_{40}]$	$[(C_6H_5)_4P]_5[BW_{12}O_{40}]$	0,04588	0,04605 ± 0,00007

Connaissant la transformation quantitative du tungstate à pH $\sim$ 2 en dodécatungstate, on a établi aussi les conditions pour le dosage des tungstates avec le chlorure de tétraphénylphosphonium.

CONDITIONS EXPÉRIMENTALES

Dosage des dodéca- et hétérododécatungstates

Le dosage de l'acide métatungstique ou de ses sels solubles s'effectue en solution 0,01–0,001*M* à chaud, 50–60°, avec une solution 0,05*M* de chlorure de tétraphénylphosphonium (la solution aqueuse du réactif a été préparée par dissolution de la substance dans l'eau: elle est stable pendant une semaine). L'exces du réactif doit être > 0,2%.

Le précipité qui se forme est filtré après refroidissement complet de la solution. Pendant ce temps le précipité amorphe se transforme en précipité cristallin. On filtre sur creuset G4 et on lave avec une solution à 0,2% de chlorure de tétraphénylphosphonium; séchage en étuve à 70–80° pendant 90–120 min.

Les dosages des hétéropolytungstates tels que $[SiW_{12}O_{40}]^{4-}$, $[PW_{12}O_{40}]^{3-}$ et $[BW_{12}O_{40}]^{5-}$ s'effectuent dans les mêmes conditions.

Dosage des tungstates

Les solutions de tungstates alcalins sont portées à pH ~ 2 (pour être transformées en dodécatungstates) en ajoutant 45–50 ml d'une solution tampon de type Clark-Lubs de pH = 2 (88,10 ml 0,2*M* KCl + 11,90 ml 0,2*M* HCl dilués à 200 ml). On fait bouillir 15–20 min; on laisse refroidir jusqu'a 50–60° et puis on continue de procéder comme pour le dodécatungstate.

Summary—A physico-chemical study of the conditions of formation (pH, time, temperature) of dodecatungstates and of their separation with tetraphenylphosphonium chloride is presented. In the iso- and heteropolytungstate series only the anions of the form $[XW_{12}O_{40}]^{(8-n)-}$ (where *n* is the oxidation number of X) are precipitated by this reagent. The reaction is quantitative and can be used to separate the dodecatungstate from a mixture of tungstate anions. By using tetraphenylphosphonium chloride as a specific reagent for dodecatungstate it has been possible to show that in the condensation of sodium tungstate in high concentrations of acid the dodecatungstate begins to appear at pH ~ 6 and all the tungstate is in this form at pH ~ 2. Factors such as dilution, time and temperature also affect the formation of dodecatungstate over this pH range. The reaction is used for the determination of a series of dodecatungstates.

Zusammenfassung—Die Bildungsbedingungen (pH, Zeit, Temperatur) von Dodekawolframaten und ihre Abtrennung mit Tetraphenylphosphoniumchlorid wurden physikalisch-chemisch untersucht. In der Iso- und Heteropolywolframat-Reihe werden nur die Anionen des Typs $[XW_{12}O_{40}]^{(8-n)-}$ (wo *n* die Oxidationszahl von X bedeutet) durch dieses Reagens gefällt. Die Reaktion ist quantitativ und kann dazu dienen, Dodekawolframat aus einem Gemisch von Wolframat-Anionen abzutrennen. Mit Tetraphenylphosphoniumchlorid als spezifischem Reagens auf Dodekawolframat ließ sich zeigen, daß bei der Kondensation von Natriumwolframat in hohen Säurekonzentrationen das Dodekawolframat bei pH ~6 auftritt und bei pH ~2 alles Wolframat in dieser Form vorliegt. Faktoren wie Verdünnung, Zeit und Temperatur sind ebenfalls von Einfluß auf die Bildung von Dodekawolframat in diesem pH-Bereich. Die Reaktion wird zur Bestimmung einer Reihe von Dodekawolframaten verwendet.

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REACTIONS OF ERIOCHROME BLUE BLACK R

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Summary—The reactions of Eriochrome Blue Black R with approximately 25 metals are tabulated. Photometric titrations of molybdenum and uranium are described, and a new method of titrating thulium with EDTA is presented.

IN 1948 Schwarzenbach[1] introduced Eriochrome Blue Black R (Calcon, C.I. 15705, previously C.I. 202) and described its properties. Since that time, this dye, "Erio R", has been suggested as an indicator for various metal–EDTA titrations, such as the determination of calcium and magnesium.[2] In order to understand the reactions of this more or less typical *o,o'*-dihydroxyazo indicator and to gain some insight into the analytical potential of this type of compound, we have compiled a summary of the reactions of Erio R. This indicator has already been the subject of some investigations,[1,2,3] but the results have not yet all appeared in the literature.

EXPERIMENTAL

All chemicals were reagent grade except lanthanum, which was "C.P", and the Erio R. Crude Erio R was obtained from the G. Frederick Smith Chemical Company of Columbus, Ohio; 3 g of it were dissolved with the aid of sodium hydroxide in 500 ml of distilled water. It was precipitated by adding 150 ml of concentrated hydrochloric acid, filtered off, and washed by stirring in distilled water; then it was redissolved and reprecipitated. It was then collected on filter paper and dried in a vacuum desiccator. Thin-layer chromatography on silica gel indicated the presence of only one coloured species in the material and it was not purified further. Standard solutions of the dye were prepared by dissolving 90–100 mg of it in a litre of distilled water. They were standardised by titrating photometrically with copper (which forms a 1:1 complex with Erio R) a 50-ml aliquot in 300–400 ml of distilled water made basic with ammonia buffer. The wavelength 635 mμ was selected for monitoring.

Combining ratios were studied by means of photometric titrations of Erio R in buffered solutions of various pH values with the metals listed in Table I. Metal titrant solutions were $\sim 10^{-2}M$. A Cary Model 14 Recording Spectrophotometer and 1-cm silica cells were used in these studies. Stability constants were determined photometrically in the visible region of the spectrum by (*a*) the Bjerrum titration method, (*b*) the molar ratio method, or (*c*) abbreviated complementary tristimulus colorimetry. The use of these methods for studying stability constants has been outlined elsewhere.[2,3,5,6] Dye factors, *i.e.*, the ratio of $[H_3A]$ to total free indicator concentration, were used when necessary to correct the photometric Bjerrum method in pH ranges where more than one form of the free dye exists. In such cases the photometric absorbance data were obtained near an isosbestic point of uncomplexed Erio R. The ionization constants[3] of tribasic Erio R (H_3A) were taken as $pK_1 = 1{\cdot}0$, $pK_2 = 7{\cdot}4$, $pK_3 = 13{\cdot}5$. Buffers were generally acetate and borate solutions except where inappropriate [*e.g.*, with lead(II)]. Low concentrations of the buffer were employed to avoid side-reactions with the metal.

RESULTS AND DISCUSSION

When a metal complex of Erio R dissociates by displacement of the metal with hydrogen ions, the reaction usually involves two protons (charges on the various species are omitted for simplicity):

$$MA + 2H = M + H_2A \qquad (1)$$

* Mound Laboratory is operated by Monsanto Research Corporation for the U.S. Atomic Energy Commission under Contract No. AT-33-1-GEN-53.

The molar ratio method for ascertaining equilibrium constants, as applied here, is not capable of giving information on the number of protons involved in the dissociation reaction. Therefore this method was used only in cases where an excess of the metal caused the Erio R to precipitate and made the other methods inconvenient or impractical. In such cases, the reaction was assumed to involve two protons as

TABLE I.—REACTIONS OF ERIO R

Ion	Complexes, conditions	pK	Method*	Remarks (reference)
Al^{3+}	1:1 pH 3–6	22·5 ± 0·5	CTC	
	2:1 pH >8			
Be^{2+}	1:1 pH <7	~12	MR	
	2:1 pH >8			
Cd^{2+}	1:1 pH <11			
	2:1 pH >11·5	10·4	BT	
Co^{2+}	2:1 pH <9	19·0	BT	100°C (3)
		(8·7)	(BT)	(CoHA = Co + HA) (3)
Cu^{2+}	1:1 pH ~9 (NH_3)	21·2	BT	(4)
Fe^{3+}	1:1 pH ~4	20·6	BT	(3)
	2:1 pH 6–9	(17–18)	(BT)	(FeA_2 = FeA + A) (3)
Ga^{3+}	Fig. (1a)	~22	CTC	
In^{3+}	1:1 pH 4–9	16·9	MR	
La^{3+}	1:1 pH 5–7	5·4	CTC	LaHA = La + HA†
	2:1 pH >8			
Mn^{2+}	1:1 pH 10	10·6	BT	0·1 $NaNO_3$ (3)
	2:1 pH 12			
Ni^{2+}	1:1 pH <10	15·4	BT	
Pb^{2+}	1:1 pH ~10	13·2	BT	0·1 $NaNO_3$
	1:2 pH >10			
Pu^{3+}	—	~17	MR	Pu-238, 0·1 $NaNO_3$
Sc^{3+}	Fig. (1b)	18·1	CTC, BT	(3)
Sm^{3+}	1:1 pH <7			
	2:1 pH >8			
Ti^{3+}	1:1 pH ~5	23·4	BT	(3)
Th^{4+}	1:1 pH 4–8	19·8	MR	
Tm^{3+}	1:1 pH ~6	5·6	CTC	TmHA = Tm + HA†
	2:1 pH >8			
UO_2^{2+}	1:1 pH 5–11	18·9	BT	
V^{3+}	1:1 pH ~5	21·7	BT	(3)
VO_2^{2+}	1:1 pH 5–10	16·3	BT	0·1 $NaNO_3$ (3)
Y^{3+}	1:1 pH <7	13·6	MR	
	2:1 pH >8			

* BT = Bjerrum titration
MR = Molar ratio
CTC = Complementary tristimulus colorimetry.
† In the presence of 0·1M α-hydroxyisobutyric acid.

described above. With some ions [*e.g.*, aluminium, iron(II), gallium(III) and cobalt(II)] reaction (1) is slow. The pK values listed in Table I are for the reaction:

$$MA = M + A \qquad (2)$$

except as noted otherwise. These were calculated from the measured equilibrium constant of reaction (1), and the second and third ionization constants of Erio R. Table I lists the pK values for reaction (2), and the combining ratio of Erio R with the metals under various conditions of pH. A complex containing two Erio R ions per metal ion is designated 2:1. Methods (*a*), (*b*), and (*c*) are abbreviated BT, MR

and CTC. Stability constants were determined in the presence of 0·1*M* sodium chloride except as noted.

In addition to the elements listed in Table I, arsenite, potassium niobate, and rhodium(III) chloride were investigated and found to be unreactive toward Erio R. Species which react with Erio R by undergoing reduction include iron(III), diamminosilver(I), mercury(II), ruthenium(IV) chloride, platinum(IV)chloride and plutonyl(VI). There is evidence of complexing with palladium(II) chloride. The indicator is precipitated even by small amounts of hafnyl and zirconyl ions, and of dicyclopentadienyl zirconium dichloride.

Perhaps the most interesting reactions of Erio R are the reactions with molybdate and tungstate. There is no evidence of reaction between Erio R and either the molybdate or the tungstate ions in basic solution. In acidic solution, however, both combine with Erio R to form a 1:1 complex. The reaction with molybdenum was studied by complementary tristimulus colorimetry at a total molybdenum concentration of about $10^{-3}M$. The reaction at this molybdenum concentration is complete near pH 4. In the equation below, the symbols [Mo] and [MoA] represent the reacting molybdenum species and the Erio R complex formed and the constant is for the complexation reaction as written.

$$[\mathrm{Mo}] + \mathrm{H_2A} + 2\mathrm{H^+} = [\mathrm{MoA}]; \qquad \log K = 13{\cdot}8.$$

Molybdenum derived from sodium molybdate or ammonium isopolymolybdate $[(NH_4)_6Mo_7O_{24}\,.\,4H_2O]$ reacts similarly. When the latter is used, seven Erio R molecules react with one isopolymolybdate species, indicating that this complex species is cleaved in solution. Molybdenum(V), prepared by reduction of molybdenum(VI) with hydrazine sulphate,[7] does not react with Erio R.

The reaction of tungsten (from Na_2WO_4) with Erio R also occurs in acidic solution, but the reaction, studied in the same manner as the molybdenum reaction, proceeds apparently by a one-proton step. For the complexation reaction $[\mathrm{W}] + \mathrm{H_2A} + \mathrm{H^+} = [\mathrm{WA}]$ the value of log K was determined to be 5·4.

From the results listed in Table I, and the discussion above, certain uses of Erio R, and possibly other hydroxyazo dyes, are suggested. These procedures are listed principally as suggestions for new avenues of research with hydroxyazo indicators.

Determination of molybdenum

To a solution containing about 10^{-5} mole of molybdenum(VI) in 300 ml of distilled water, add sufficient acid to adjust the pH to 1·5–3·0. Acetate may be used as a buffer at pH 3. Titrate photometrically with $\sim 2 \times 10^{-3}M$ Erio R (kept at pH ~4 to inhibit decomposition). The wavelength 510 mμ is best for visible photometric titrations, although at this wavelength the extrapolated end-point is not sharp because the absorbances of the chelate and uncomplexed dye do not differ greatly. The Erio R should be previously standardised against Mo(VI). Many metal ions interfere [*e.g.*, iron(III) and lead] but cadmium and lanthanum do not. Six determinations on molybdenum solutions of varying concentration gave an average deviation of $\pm 1\%$.

Estimation of uranium, plutonyl(VI) *and thulium*

The high association constant of uranium and Erio R allows uranium to be titrated photometrically with Erio R. At pH 4 in acetate buffer many metals interfere, but lead does not. The wavelength 500 mμ may be used, but at this wavelength the extrapolated end-point is not sharp. The precision of the method was not checked.

The bivalent plutonyl(VI) ion acts as an oxidant toward Erio R, and this property may be used to estimate its concentration in solution at pH 3. The photometric titration may be carried out at 510 mμ. The method is only approximate for the 238 isotope because of extensive valence wandering.[8]

Erio R has not been suggested for the direct titration of the rare earths with EDTA. We have

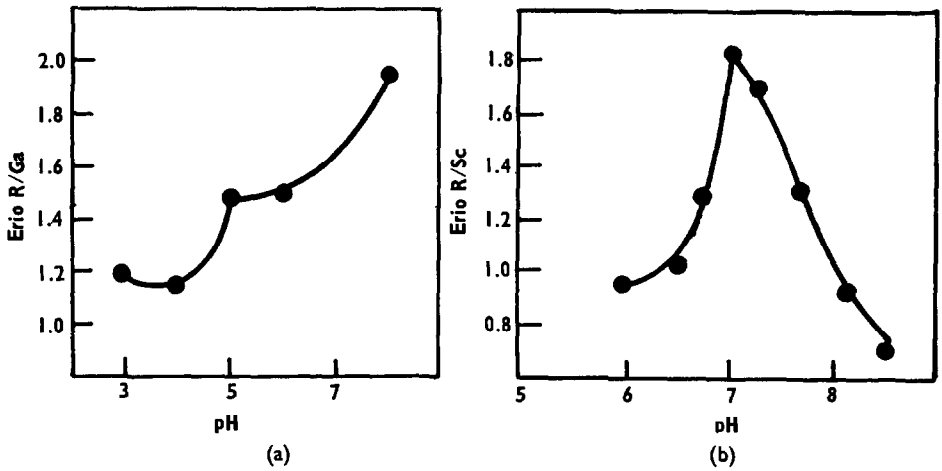

FIG. 1.—Apparent ratio of Erio R to (a) gallium and (b) scandium as a function of pH.[3]

found that 10^{-5} mole of thulium in 50 ml of solution to which has been added 10^{-3} mole of α-hydroxyisobutyric acid can be titrated visually in ammonia buffer (pH 8–9) with $10^{-2}M$ EDTA. The change at the end-point is from purple to sky-blue. Six determinations gave an average deviation of less than 2%.

Zusammenfassung—Die Reaktionen von Eriochromschwarz R mit etwa 25 Metallen werden tabelliert. Photometrische Titrationen von Molybdän und Uran sowie eine neue Methode zur Titration von Thulium mit EDTA werden beschrieben.

Résumé—On a répertoirié les réactions du Bleu Noir d'Eriochrome R avec environ 25 métaux. On décrit les dosages photométriques du molybdène et de l'uranium, et présente une nouvelle méthode de dosage du thulium avec l'EDTA.

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APPLICATION DES COURBES DE VOLATILISATION-EXCITATION A LA DETERMINATION DES CONDITIONS DE L'ANALYSE SPECTROCHIMIQUE DE L'OXYDE DE TANTALE

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Résumé—La détermination des conditions spectrographiques optimales pour l'analyse de l'oxyde de tantale est facilitée par la considération des courbes de volatilisation des éléments recherchés. La méthode est appliquée au dosage de Cr, Fe, Hf, Ni, Nb, Ti, Y et Zr à des concentrations de l'ordre de 10 à 1000 ppm.

UN MÉCANISME des réactions chimiques survenant au niveau des électrodes de graphite utilisées en spectrographie d'arc sur oxydes a été suggéré antérieurement.[1] Les conclusions énoncées s'appuyaient sur l'examen de "courbes de volatilisation-excitation"† qui, selon l'élément considéré (ou plutôt la combinaison dans laquelle il se trouve engagé), revêtent l'une des allures, monotones et décroissantes (type A), ou présentant un minimum (type B), des courbes de la Fig. 1.

La considération de ces courbes est appliquée dans ce qui suit à la détermination des conditions opératoires optimales pour le dosage de Cr, Fe, Hf, Ni, Nb, Ti, Y et Zr dans l'oxyde de tantale, sujet qui n'a été abordé que par de rares auteurs dont particulièrement Laib.[2]

Supposons construite la courbe de volatilisation-excitation, relative à une raie d'un des éléments à doser; soit t_1 le temps de préflambage et t_2 le temps d'exposition, les autres conditions expérimentales étant supposées définies. En première approximation, et sous certaines conditions, le noircissement de la plaque sous l'effet de la radiation pourra être considéré comme proportionnel à la surface comprise entre la courbe de vaporisation-excitation, l'axe des temps et les deux droites paralleles à l'axe des ordonnées d'abscisses t_1 et t_2.

Dans la pratique, on pourra ainsi sélectionner une raie analytique, optimaliser les temps de préflambage et d'exposition, déterminer l'intensité de l'arc, en fonction de la sensibilité recherchée. De même, il devient possible, dans certains cas, de réduire l'intensité d'une raie parasite, de déterminer les conditions dans lesquelles l'application de la méthode dite "de l'étalon interne" est licite, *etc.*

PARTIE EXPERIMENTALE

Construction des courbes de volatilisation-excitation des éléments à doser

Ce travail a été fait dans les conditions générales déjà exposées et rappelées ci-dessous.
Générateur d'arcs continus.
Electrode cratère positive inférieure emplie d'un
Mélange de 1 partie d'oxyde avec 1,25 partie de graphite.
Spectrographe Optica B 5 (équipé d'un réseau de 2160 tr/mm fournissant une dispersion inverse de 3,6 Å/mm).
Plaques: Kodak B 10.

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† Les courbes expriment, pour une radiation déterminée, l'énergie lumineuse reçue par la plaque en fonction de l'âge de l'arc; on peut, dans l'application courante, se contenter de porter en ordonnée la mesure de la densité optique ainsi qu'il ressort de l'exposé fait dans.[1]

Les données relatives aux 40 courbes construites figurent au Tableau I.

TABLEAU I.—CONDITIONS D'OBTENTION DES COURBES DE VOLATILISATION-EXCITATION

Elément	Taux, %	Raie spectrale, Å		Excitations, Å	Type de la courbe
Cr	0,1	4254,3	I	*10*	A
Fe	0,1	*3020,6*	I	2–4–*10*	A
		2599,4	II	14–21	
Hf	1.0	*2773,4*	II	5–*10*–14	B
		2783,7	I	10	
Nb	1,0	*3094,2*	II	2–4–*10*–14	B
		3225,5	II	5–*10*–14	
Ni	0,1	3050,8	I	*10*	A
Ta	Matrice	2594,3	II	5–*10*–14	B
Ti	1,0	*3078,6*	II	2–4–*10*–14	B
		3106,2	II	5–10–14	
Y	0,2	3195,6	II	10–21	
		4309,6	II	10–14–21	A*
		4374,9	II	10–14–21	
Zr	1,0	2799,1	II	10	B
		3306,3	II	5–10–14	

* Les courbes relatives à l'Y accusent, sous certaines conditions, une légère remontée qui les apparente à celles du type B.

N.B. Les valeurs en italique ont été retenues pour le protocole opératoire (*cf.* Tableau 3).

Chaque courbe est construite à l'aide de deux séries indépendantes de 13 points correspondant à des poses de 5 sec espacées de 5 sec, durant lesquelles la plaque est déplacée (Moving Plate Method).

Les courbes relatives à une raie de chacun des 4 éléments Hf, Nb, Ni et Ti, sont représentées Fig. 1 à titre d'exemple; elles correspondent à des arcs d'une intensité de 10 A, qui sont ceux qui ont donné les dispersions minimales.

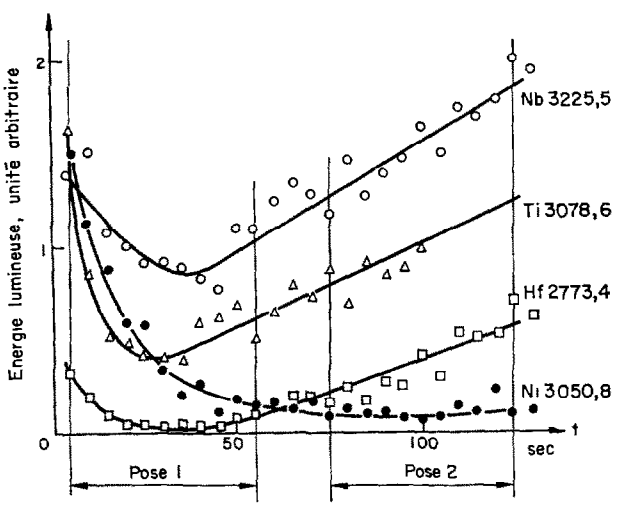

FIG. 1.—Courbes de volatilisation-excitation de Hf, Nb, Ni et Ti.

La recherche de la sensibilité a conduit à considérer successivement, comme il ressort de l'observation de ces courbes, deux temps de pose de 50 sec décalés de 20 sec l'un par rapport à l'autre: ainsi, les éléments présentant des courbes de type A, soit Cr, Fe, Ni (et Y), sont dosés à l'aide d'une première exposition après un préflambage de 5 sec. Les autres éléments, soit Hf, Nb, Ti et Zr, sont dosés à l'aide d'une seconde pose prise au cours de la même décharge, mais dont le début a lieu 75 sec après l'amorçage de l'arc.

Le Tableau II exprime, avec une unité arbitraire commune, l'intensité relative des 4 raies de la Fig. 1, d'une part pour la pose 1 ($t_1 = 5$ sec, $t_2 = 50$ sec), d'autre part pour la pose 2($t_1 = 75$ sec, $t_2 = 50$ sec).

TABLEAU II.—INTENSITES RELATIVES ESCOMPTÉES DES RAIES DE Hf, Nb, Ni, Ti

Conditions de pose (*cf.* Fig. 1)	Hf	Nb	Ni	Ti
1	2	26	14	16
2	11	40	3	21

Courbes d'étalonnage

La sensibilité souhaitée, des interférences gênantes et la recherche d'un compromis entre la grande dispersion du spectrographe et l'utilisation d'une plage restreinte de longueurs d'onde, nous ont conduits dans la pratique: à adopter les raies et les conditions opératoires du Tableau III; à disjoindre le cas de l'ytrium qui fera l'objet d'une détermination séparée (ainsi qu'il ressort du même tableau). La Fig. 2 reproduit les courbes d'étalonnage obtenues à l'aide d'étalons préparés par mélanges directs d'oxydes.

TABLEAU III.—CONDITIONS OPÉRATOIRES ET LIMITES DE DÉTECTION

Element	Raie analytique, Å	Excitation, *A*	t_1, *sec*	t_2, *sec*	Limite de dosage, *ppm*
Cr	3021,6	10	5	50	10
Fe	3020,6	10	5	50	10
Ni	3414,7	10	5	50	10
Hf	2773,4 ou 3399,8	10	75	50	700
Nb	3225,5 ou 3094,2	10	75	50	100
Ti	3078,6	10	75	50	60
Zr	3392,0	10	75	50	100
Y	3242,3	14	5	90	5

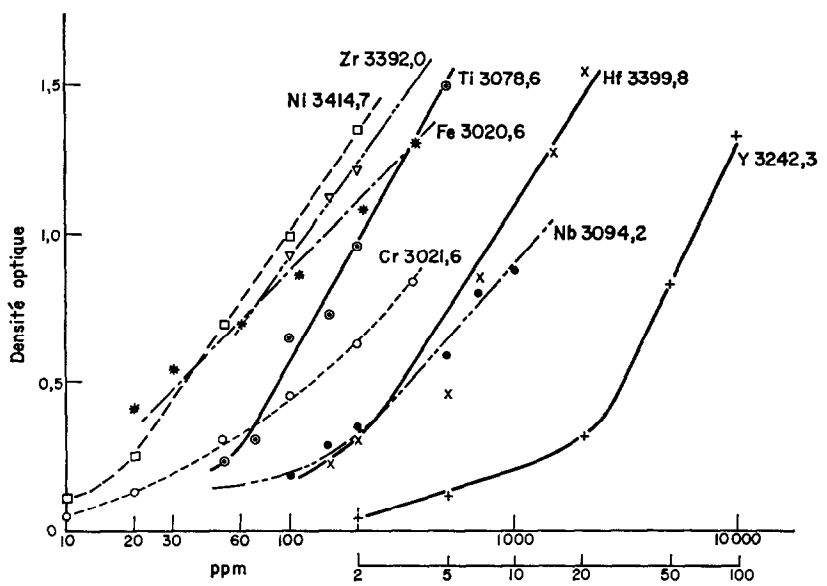

FIG. 2.—Courbes d'étalonnage.

DISCUSSION ET CONCLUSION

L'exemple précédent d'utilisation des courbes de volatilisation-excitation à des fins analytiques en montre l'intérêt. Le travail nécessité par le tracé de ces courbes, qui illustrent la cinétique du processus global (thermochimique et électronique) mis en oeuvre, peutêtre substantiellement allégé: en effet, les raies de même nature d'un atome présentent des courbes très semblables et on pourra fréquemment se dispenser de les tracer pour de nombreuses longueurs d'onde.

Cependant, la comparaison de courbes relatives à des raies d'intensité très différente ne devra se faire qu'après avoir fait correspondre aux noircissements les énergies incidentes correspondantes, ceci afin de tenir compte au plus près des phénomènes photographiques. Cette remarque prend toute sa valeur lors de l'utilisation analytique d'une raie forte dans le but d'accroître la sensibilité, alors que ce sont les courbes relatives à des raies plus faibles qui ont été tracées à l'aide de substances de concentration beaucoup plus élevées en l'élément recherché. La même remarque est à considérer lors de la recherche de l'intensité optimale d'excitation.

Summary—The determination of the optimum conditions for the spectrographic analysis of tantalum oxide is facilitated by consideration of the volatilization curves for the elements sought. The method is applied for the estimation of Cr, Fe, Hf, Ni, Nb, Ti, Y and Zr at the 10–1000 ppm level.

Zusammenfassung—Die Ermittlung der optimalen Bedingungen zur spektrographischen Analyse von Tantaloxid wird erleichtert durch Betrachtung der Verflüchtigungskurven der gesuchten Elemente. Die Methode wird angewandt auf die Bestimmung von Cr, Fe, Hf, Ni, Nb, Ti, Y und Zr bei 10–1000 ppm.

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POTENTIOMETRIC STUDY OF COMPLEXES OF LEAD(II) WITH DITHIOCARBAMINOACETIC ACID

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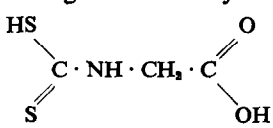
Summary—A potentiometric determination of the stability constants of lead(II)–dithiocarbaminoacetic acid complexes has been made. Potentiometric data have been used for estimating the maximum number of co-ordinated ligands. After graphical solution of the Fronaeus integral, the relationship between the concentration variables has been found, and the curve-fitting method, in which both variables are normalised, has been used for determining the stability constants. The values found are $\log \beta_1 = 7{\cdot}32 \pm 0{\cdot}12$ and $\log \beta_2 = 13{\cdot}03 \pm 0{\cdot}20$ ($\mu = 0{\cdot}1$; 25°). From these data, the relationship between the conditional stability constant $\log \beta_2'$ and pH has been calculated, thus furnishing a full description of TCA as a masking agent for lead ions.

DITHIOCARBAMINOACETIC acid (TCA) forms very stable water-soluble complexes with a number of metal ions.[1–3] Although the stability constants of the complexes have



(TCA)

not been determined, our preliminary qualitative investigations showed that they follow a sequence corresponding to the solubility of the metal sulphides. This fact was used in the application of TCA as a new masking agent in complexometry.[4]

For wider and more expedient use of TCA in analytical chemistry, the stability constants must be known. This paper describes an attempt to determine the stability constants of lead(II) TCA complexes by a potentiometric method with an amalgam electrode. The potentiometric determination of the acid dissociation constants of TCA[5] and the spectrophotometric determination of the stability constants of cobalt(II) TCA complexes[6] have previously been reported.

EXPERIMENTAL

Symbols[7]

A—total concentration of ligand A.
a—concentration of free ligand.
B—total concentration of central group B.
b—concentration of free central group.
h—concentration of free hydrogen ions.
n—number of ligands in mononuclear complex BA_n.
N—maximum value of n.
$\bar{n} = (A - a)/B$—average number of ligands A bound to one central group B.
$\alpha_c = [BA_c]/B$—fraction of B in form of BA_c.
$\beta_n = [BA_n]/ba_n$—over-all concentration stability constant.
$\beta_j^H = [H_jA]/ah^j$—over-all proton stability constant.

Apparatus

Measurements were carried out in such a manner that the concentration b of the free central group was determined as portions of ligand A were added.

The galvanic cell

$Hg\text{-}Hg_2Cl_2$	satd. KCl soln.	$0{\cdot}1M$ KNO_3	$0{\cdot}01M$ formate buffer $0{\cdot}09M$ KNO_3 $x.10^{-4}M$ $Pb(NO_3)_2$ $y.10^{-4}M$ TCA	Hg-Pb

consisted of an amalgam electrode, reversible with respect to the concentration of free metal ions, and a saturated calomel electrode (SCE) as a reference half-cell.

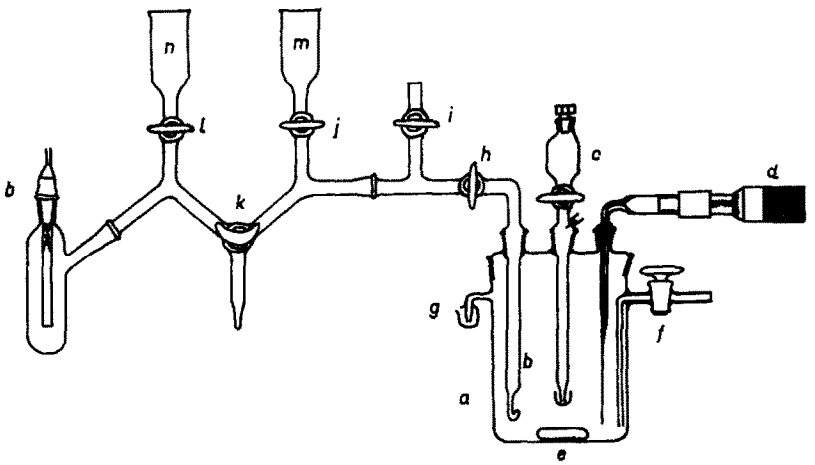


FIG. 1.—The apparatus for potentiometric titration with an amalgam electrode.

The apparatus (shown in Fig. 1) was prepared for measurements as follows: a solution of known concentration B was placed in the vessel a. The holes in the glass cover were closed with glass stoppers. Through the cock f and the water-trap g, a stream of very pure nitrogen (99·999%), saturated with water vapour, was passed through the solution. The apparatus was kept in an air-thermostat at 25 ± 0·1°. The salt-bridge was filled with potassium chloride solution (saturated at 25°) by means of the vessel n and the stop-cocks k and l; the right-hand side of the bridge was filled with $0{\cdot}1M$ potassium nitrate solution through the vessel m and the stop-cocks k, j, i and h. The amalgam in the lower part of the amalgam electrode was replaced with fresh and the electrode was put in the vessel a. The amalgam in the upper part of the electrode was kept under a layer of liquid paraffin. Just before measurements were started, the stop-cocks k and h were opened. In this way conditions for very reproducible contact between the two solutions were realized. The solution in the vessel a was stirred with a magnetic stirrer e. Portions of the $0{\cdot}1M$ solution of the ligand were added from the microburette d. The potential of the amalgam electrode was measured with a potentiometer with a precision of ±0·05 mV. The potentiometer was checked with a Weston standard cell.

Preliminary investigations

First, the dependence of the potential of the amalgam electrode on the concentrations of lead ions in the absence of complexing agents was determined. Experiments showed that in the concentration range 10^{-3}–$10^{-4}M$, the relationship E/-log $[Pb^{2+}]$ is linear and has approximately the theoretical slope of ~28 mV. Because TCA is the conjugate base of a weak acid, measurements with it were carried out in the presence of buffer. Formic acid forms very weak complexes with lead ions ($\log \beta_1 = 0{\cdot}78$, $\log \beta_2 = 1{\cdot}20$, $\log \beta_3 = 1{\cdot}43$ and $\log \beta_4 = 1{\cdot}18$),[8] so a formate buffer will not noticeably interfere. This was confirmed by our experiments, which showed that the alteration of the potential $0{\cdot}01M$ formic acid was added was negligible (about 0·5 mV). Our measurements were carried out in the presence of $0{\cdot}01M$ potassium formate–formic acid buffer solution, pH = 4 ± 0·05.

Measurements and data processing

A series of experiments was performed with the equipment described and the course of the complexation reaction was followed. Difficulties arose from appearance of a precipitate when a portion of ligand A was added, but if $10^{-4}M$ lead was used the solution remained clear throughout.

TABLE I.—DATA OF A, E, α_0, $\bar{n}$, a OBTAINED FROM ONE EXPERIMENT. CONDITIONS: $B = 1{\cdot}10^{-4}$ M $Pb(NO_3)_2$; 0·01 M FORMIATE BUFFER pH = 4·00 ± 0·05; VOLUME 25 ml; IONIC STRENGTH μ = 0·1 (KNO_3); 25 ± 0·2°C; TITRATED WITH 0·1 M TCA.

A	E, mV	α_0	$\bar{n}$	a
—	427·4	—	0·00	—
$1{\cdot}56 . 10^{-5}$	430·0	$8{\cdot}00 . 10^{-1}$	0·16	—
$3{\cdot}12 . 10^{-5}$	432·0	$6{\cdot}80 . 10^{-1}$	0·31	—
$6{\cdot}25 . 10^{-5}$	439·6	$3{\cdot}50 . 10^{-1}$	0·63	$1{\cdot}13 . 10^{-7}$
$7{\cdot}80 . 10^{-5}$	444·4	$2{\cdot}40 . 10^{-1}$	0·78	$2{\cdot}02 . 10^{-7}$
$1{\cdot}17 . 10^{-4}$	461·5	$5{\cdot}50 . 10^{-2}$	1·17	$9{\cdot}66 . 10^{-7}$
$1{\cdot}40 . 10^{-4}$	474·5	$1{\cdot}78 . 10^{-2}$	1·40	$2{\cdot}37 . 10^{-6}$
$1{\cdot}64 . 10^{-4}$	488·4	$5{\cdot}50 . 10^{-3}$	1·64	$4{\cdot}96 . 10^{-6}$
$1{\cdot}87 . 10^{-4}$	499·6	$2{\cdot}34 . 10^{-3}$	1·87	$8{\cdot}41 . 10^{-6}$
$2{\cdot}18 . 10^{-4}$	518·3	$4{\cdot}27 . 10^{-4}$	2·00	$2{\cdot}06 . 10^{-5}$
$2{\cdot}34 . 10^{-4}$	525·2	$2{\cdot}40 . 10^{-4}$	2·00	$2{\cdot}79 . 10^{-5}$
$2{\cdot}58 . 10^{-4}$	535·4	$1{\cdot}00 . 10^{-4}$	2·00	$4{\cdot}22 . 10^{-5}$
$2{\cdot}89 . 10^{-4}$	544·6	$4{\cdot}47 . 10^{-5}$	2·00	$6{\cdot}38 . 10^{-5}$
$3{\cdot}51 . 10^{-4}$	556·9	$1{\cdot}58 . 10^{-5}$	2·00	$1{\cdot}08 . 10^{-4}$
$4{\cdot}05 . 10^{-4}$	565·5	$7{\cdot}47 . 10^{-6}$	2·00	$1{\cdot}53 . 10^{-4}$
$4{\cdot}68 . 10^{-4}$	572·0	$4{\cdot}37 . 10^{-6}$	2·00	$2{\cdot}06 . 10^{-4}$
$5{\cdot}85 . 10^{-4}$	581·2	$2{\cdot}00 . 10^{-6}$	2·00	$3{\cdot}02 . 10^{-4}$
$7{\cdot}03 . 10^{-4}$	588·4	$1{\cdot}07 . 10^{-6}$	2·00	$4{\cdot}12 . 10^{-4}$
$1{\cdot}56 . 10^{-3}$	614·4	$1{\cdot}18 . 10^{-7}$	2·00	$1{\cdot}25 . 10^{-3}$
$2{\cdot}03 . 10^{-3}$	622·1	$6{\cdot}17 . 10^{-8}$	2·00	$1{\cdot}72 . 10^{-3}$
$3{\cdot}12 . 10^{-3}$	634·3	$2{\cdot}14 . 10^{-8}$	2·00	—

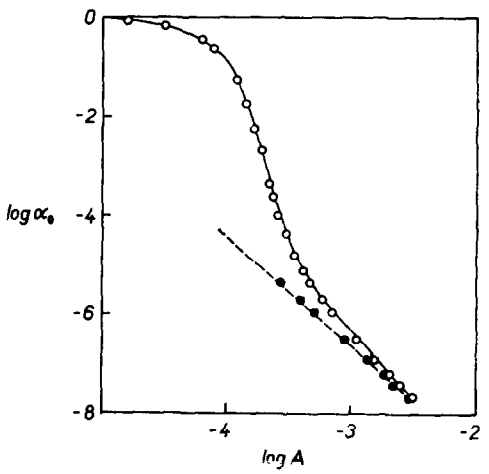


FIG. 2.—Dependence of log α_0 on the total amount of TCA added.

From the relationships[7]

$$(E)_A = E_0' - \frac{RT}{zF} \ln b \qquad \text{and} \qquad (E)_{A=0} = E_0' - \frac{RT}{zF} \ln B \tag{1}$$

we calculated

$$(\Delta E)_B = (E)_{A=0} - (E)_A = \frac{RT}{zF} \ln \frac{b}{B} = 0{\cdot}028 \log \alpha_0, \tag{2}$$

where E is the potential of the system, E_0 is the standard electrode potential and z is the number of electrons involved in the electrode reaction.

By measuring the potential of the amalgam electrode before and after the addition of the ligand, the relationship between log α_0 and log A was found (see Table I and Fig. 2). Under the chosen

conditions the value of the liquid–junction potential was negligible, but in any case it is evident from equation (2) that the liquid–junction potential is eliminated.

From the well-known relationship between the secondary concentration variables[7,9]

$$\frac{\mathrm{d}\log\alpha_0}{\mathrm{d}\log a} = -\bar{n} \tag{3}$$

the value of $\bar{n}$ can be obtained. In our case, we do not measure directly the function $\log\alpha_0/\log a$; however, when the ligand is in excess, the approximation

$$\frac{\mathrm{d}\log\alpha_0}{\mathrm{d}\log A} \approx \frac{\mathrm{d}\log\alpha_0}{\mathrm{d}\log a} = -N \tag{4}$$

can be used.

As our experiments were not carried out with an extremely large excess of the ligand, we did not obtain a precise meaning for the maximum value of N from equation (4) (the result obtained was $N' = 2{\cdot}55$, see Fig. 2—open circles). To have a more precise value for a, we used the relationship

$$a = A - N'B \tag{5}$$

from which a number of a values were calculated. Then the more precise relationship of $\log\alpha_0$ to $\log a$ was obtained, from which a better value, N, was determined. The N–a pairs were then refined by successive approximation until convergence was obtained. The number of co-ordinated ligands finally found is $N = 2$ (see Fig. 2—black circles).

For the calculation of the stability constants β_1 and β_2, knowledge of the relationship between α_0 and a was needed. It was found by solving the Fronaeus integral.[7,10]

From equation (3),

$$\log a_1 = -\int\frac{1}{\bar{n}}\,\mathrm{d}\log\alpha_0 + \log a_2 \tag{6}$$

where a_1 is the unknown value of the free ligand concentration, a_2 is the known value of free ligand concentration, calculated from (5) for the case in which the ligand is in excess ($A \gg B$). The Fronaeus integral was solved graphically by drawing the function $(1/\bar{n})$ $(-\log\alpha_0)$ and using the approximation

$$\bar{n} \approx \frac{A}{B} \tag{7}$$

in the region $A < NB$, the complexes being very stable. The approximation $\bar{n} \approx N$ was used in the region $A > NB$ (see Fig. 3). After solution of the Fronaeus integral, the rigorous values of a were used to refine the approximation (7), by means of the exact expression

$$\bar{n} = \frac{A - a}{B} \tag{8}$$

The $\bar{n}$ and a values were refined by successive approximation with equation (6) and (8) until convergence was obtained (see Fig. 3—closed circles).

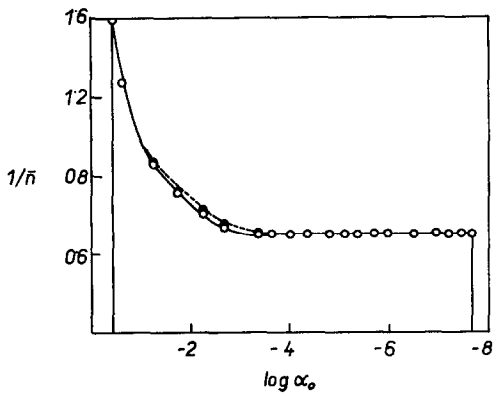


FIG. 3.—Graphical solution of the Fronaeus integral.

The stability constants were computed from α_0 and a values by Sillén's curve-fitting method, in which the two variables were normalised.[11] More details of this method can be found in Rossotti and Rossotti's excellent book on the determination of stability constants.[7] In Fig. 4, is shown a plot of log $(B - b)/ba$ *vs.* log a with data obtained from four experiments. Experiments were performed with various concentrations of the total central group B, and the results show that the complex is mononuclear.

As measurements were carried out at constant pH, the stability constants are conditional (or apparent). The concentration stability constants were found by using the α_H factor

$$\beta_1 = \beta_1'(1 + \beta_1^H h + \beta_2^H h^2) \tag{9}$$

$$\beta_2 = \beta_2'(1 + \beta_1^H h + \beta_2^H h^2)^2 \tag{10}$$

where β_1' and β_2' are the corresponding conditional constants and $\beta_1^H = 5{\cdot}6 \times 10^3$ and $\beta_2^H = 4{\cdot}7 \times 10^6$ are the proton stability constants of TCA, determined at 25° and ionic strength 0·1. The values for β_1 and β_1 found here are

$$\log \beta_1 = 7{\cdot}32 \pm 0{\cdot}12 \qquad \beta_1 = (2{\cdot}1 \pm 1{\cdot}3) \times 10^7$$

$$\log \beta_2 = 13{\cdot}03 \pm 0{\cdot}20 \qquad \beta_2 = (1{\cdot}1 \pm 1{\cdot}6) \times 10^{13}$$

where the limits of error are the permissible vertical and horizontal displacements of the origin of the normalized curve.

For a fuller description of the complexation reaction it was necessary to know the stability constants of mixed hydrogen and hydroxo complexes of type BH_jA_n and $B(OH)_jA_n$. To achieve this, we used Sillén's[7,12] method of obtaining the relationship between two of the free concentration variables

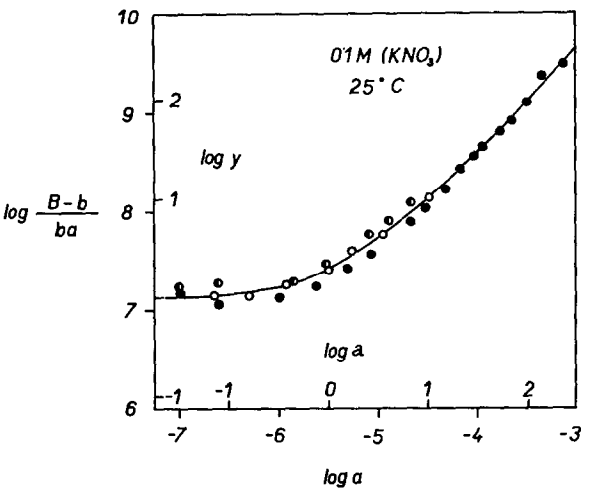


FIG. 4.—The experimental data for log $(B - b)/ba$ as a function of log a for the lead(II)–TCA system, superimposed on the normalised curve for log a as a function of log y.

for a series of constant values of the third. For a mononuclear system of complexes the total concentration of the central group is given by the expression

$$B = b + b \sum_0^j \sum_1^N \beta_{1jn} h^j a^n \tag{11}$$

and then

$$F_1 = \frac{B - b}{ba} = \sum_0^j \sum_1^N \beta_{1jn} h^j a^{n-1} = \sum_1^N \Phi_n a^{n-1} \tag{12}$$

where the function

$$\Phi_n = \sum_0^j \beta_{1jn} h^j$$

is constant at a given hydrogen ion concentration.

Thus the relationship between Φ_n and h at different pH values can be defined and the various stability constants can be found. The analysis of the function $\Phi_n(h)$ shows that Φ_1 and Φ_2 are independent of variation in h, which is a proof that in the region investigated (pH 4–9) no mixed hydrogen or hydroxo complexes are present.

DISCUSSION

Because of the stepwise complex formation, TCA can be used only for masking and not as a titration agent in spite of the high stability of its lead ion complexes. The relationship between the conditional stability constant β_2' and the pH value of the solution gives a good idea of the masking efficiency of TCA. It is the β_2' and not the β_1' constant that is the more useful, because a masking agent is added in excess and so provides conditions for the formation of the complex with the maximum co-

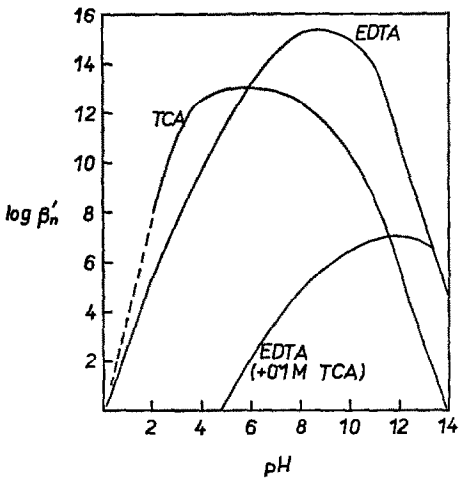


FIG. 5.—The pH-dependence of the conditional stability constant log β_2' for the Pb(TCA) complex and of log β_1' for the Pb-EDTA complex in the presence and absence of TCA.

ordination number. The relationship between log β_2' and pH was calculated according to Ringbom,[13] with data from the present paper (see Fig. 5). Depending on the acidity of the solution, TCA decomposes more or less rapidly at pH < 2, so values for this pH-region are shown by a dashed line. The β_2' values at pH > 9 are calculated without taking into consideration the possible co-existence of mixed hydroxo complexes. This factor would probably not improve the masking efficiency of TCA in the pH region mentioned. As can be seen from Fig. 5, the conditional constant β_2' reaches a maximum value between pH 4 and 8. Thus TCA can successfully be used as a masking agent for lead ions in this pH-region.

This can be illustrated in complexometry, by comparison of the conditional constant for lead–EDTA in the presence and absence of TCA, as a function of pH. The course of the two curves plotted in Fig. 5 shows that the masking efficiency of TCA will be higher at pH 3–5, where the lead–EDTA conditional constant in the presence of TCA is rather low. In basic solution TCA can be used less successfully because the conditional constant of the lead–EDTA complex even in the presence of TCA has a value 10^6–10^7. This fact is in a good agreement with former data concerning the application of TCA as a masking agent in complexometry.[4]

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Zusammenfassung—Die Stabilitätskonstanten von Blei(II) dithiocarbaminoessigsäure-Komplexen wurden potentiometrisch bestimmt. Die potentiometrischen Daten wurden zur Ermittlung der maximal koordinierten Ligandenzahl verwendet. Nach graphischer Lösung des Fronaeus-Integrals wurde die Beziehung zwischen den Konzentrationsvariablen gefunden; die Stabilitätskonstanten wurden mit der Kurvenanpassungs-Methode ermittelt, bei der beide Variablen normiert sind. Gefunden wurden $\log \beta_1 = 7{,}32 \pm 0{,}12$ und $\log \beta_2 = 13{,}03 \pm 0{,}20$ ($\mu = 0{,}1$; 25°). Aus diesen Daten wurde die Beziehung zwischen der Stabilitätskonstante $\log \beta_2$ und dem pH-Wert ermittelt; damit ist TCA als Maskierungsmittel für Blei-Ionen voll charakterisiert.

Résumé—On a effectué une détermination potentiométrique des constantes de stabilité des complexes plomb (II)-acide dithiocarbaminoacétique. On a utilisé les données potentiométriques pour estimer le nombre maximal de ligands coordinnés. Après résolution graphique de l'integrale de Fronaeus, on a trouvé la relation entre les variables de concentration et utilisé la méthode d'ajustage des courbes, dans laquelle les deux variables sont normalisées, pour déterminer les constantes de stabilité. Les valeurs trovées sont $\log \beta_1 = 7{,}32 \pm 0{,}12$ et $\log \beta_2 = 13{,}03 \pm 0{,}02$ ($\mu = 0{,}1$; 25°). De ces données, on a calculé la relation entre la constante de stabilité conditionnelle $\log \beta_2$ et le pH, fournissant ainsi une description complète du TCA en tant qu'agent de dissimulation pour les ions plomb.

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METAL CHELATE EXCHANGE IN THE ORGANIC PHASE—I

THEORY: APPLICATION IN SPECTROPHOTOMETRY AND COMPLEX CHEMISTRY

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Summary—Metal chelates, extracted from an aqueous phase by organic solvents, can react with other chelating agents (or their metal chelates) dissolved in the same solvent. This exchange of metal chelates in the organic phase can be used for (1) investigation of the exchange equilibrium and composition of the metal chelates formed, (2) determination of the extraction constants, (3) preparation of new inner-complexes soluble in organic solvents, and (4) spectrophotometric determination of small amounts of metals. The theory and experimental verification of this phenomenon are given. The extraction constants of silver and zinc diethyldithiocarbamates in carbon tetrachloride have been determined by means of the extraction constants of the corresponding dithizonates. A mixed complex of arsenic(III) with dithizone and diethyldithiocarbamic acid has been prepared and its properties studied. A simple method for spectrophotometric determination of microgram quantities of arsenic is proposed.

EXTRACTED metal chelates can be easily transformed into other metal chelates by addition of a suitable chelating agent directly to the separated organic layer. As an example the following simple experiment can be considered. To a golden-yellow solution of silver dithizonate in carbon tetrachloride a colourless solution of diethyldithiocarbamic acid in the same solvent is added; emerald green dithizone is immediately liberated. The chemical reaction which takes place can be described by the equation

$$\underset{\text{golden-yellow}}{(AgHDz)_{CCl_4}} + \underset{\text{colourless}}{(HDDC)_{CCl_4}} = \underset{\text{colourless}}{(AgDDC)_{CCl_4}} + \underset{\text{green}}{(H_2Dz)_{CCl_4}} \quad (1)$$

Similarly, by addition of diethyldithiocarbamic acid, dithizone can be liberated from zinc dithizonate*

$$\underset{\text{red}}{Zn(HDz)_2} + \underset{\text{colourless}}{2HDDC} = \underset{\text{colourless}}{Zn(DDC)_2} + \underset{\text{green}}{2H_2Dz} \quad (2)$$

and as a result of this reaction the colour of the solution rapidly changes from red to green. The same applies for other dithizonates. The amount of dithizone liberated depends on the amount of diethyldithiocarbamic acid added and on the nature of the metal complex involved.

* In this and all further equations, subscripts CCl_4 are generally omitted for sake of simplicity.

Further, when different metal chelates are mixed, *e.g.*, zinc diethyldithiocarbamate and silver dithizonate, an exchange reaction between the metal chelates immediately takes place:

$$\underset{\text{colourless}}{Zn(DDC)_2} + 2\underset{\text{yellow-orange}}{AgHDz} = \underset{\text{red}}{Zn(HDz)_2} + 2\underset{\text{colourless}}{AgDDC}. \qquad (3)$$

Similar reactions occur not only between various dithizonates and diethyldithiocarbamates but also between thio-oxinates and dithizonates, thio-oxinates and diethyldithiocarbamates, dithizonates and cupferrates, dithizonates and oxinates, *etc.*, in carbon tetrachloride and chloroform.

The exchange of metal chelates in the organic phase could have considerable analytical value. Thus if some other suitable chelating agent (or metal chelate) dissolved in the same solvent were added to a colourless extract of a metal chelate the change of colour would enable the metal in question to be determined spectrophotometrically. However, for development of such an analytical procedure not only must the colour of metal chelates involved be known but also the chemical equilibria and species formed.

For this purpose a general theory of metal chelate exchange has been developed which enables one to choose the most suitable colour-forming reagent and to study the composition of species produced by such chemical reactions. The theory has been tested by exchange reactions between metal dithizonates and diethyldithiocarbamates.

THEORETICAL

According to equation (1) the equilibrium constant of the exchange reaction between silver dithizonate and diethyldithiocarbamic acid can be expressed as:

$$E_{AgHDz-HDDC} = \frac{[AgDDC][H_2Dz]}{[AgHDz][HDDC]} = \frac{K_{AgDDC}}{K_{AgHDz}} \qquad (4)$$

where

$$K_{AgDDC} = \frac{[AgDDC]_{org}[H^+]_{aq}}{[Ag^+]_{aq}[HDDC]_{org}}$$

and

$$K_{AgHDz} = \frac{[AgHDz]_{org}[H^+]_{aq}}{[Ag^+]_{aq}[H_2Dz]_{org}}$$

are the extraction constants of silver diethyldithiocarbamate and silver dithizonate respectively. From the above it follows that the values of the exchange constants, E, can be generally used for calculation of extraction constants and *vice versa*.

Similarly, for equation (3)

$$E_{Zn(DDC)_2-AgHDz} = \frac{[Zn(HDz)_2][AgDDC]^2}{[Zn(DDC)_2][AgHDz]^2} = \frac{K_{Zn(HDz)_2}K^2_{AgDDC}}{K_{Zn(DDC)_2}K^2_{AgHDz}}$$

$$= \frac{E^2_{AgHDz\text{-}HDDC}}{E_{zn(HDz)_2-HDDC}} \qquad (5)$$

For the general case, an exchange reaction between metal chleate, MA_n, and chelating agent, HB, can be described as

$$MA_n + nHB = MB_n + nHA \qquad (6)$$

with an exchange constant

$$E_{MA_n-HB} = \frac{[MB_n][HA]^n}{[MA_n][HB]^n} = \frac{K_{MB_n}}{K_{MA_n}} \quad (7)$$

Thus for a quantitative transformation of MA_n to MB_n (*i.e.*, $[MB_n]/[MA_n] > 100$) it is necessary that $E_{MA_n-HB}\{[HB]^n/[HA]^n\} > 100$. Therefore, when a tenfold excess of colour-forming reagent HB is applied the value of E_{MA_n-HB} for $n = 1$, 2, 3 and 4 should be greater than 10, 1, 0·1 and 0·01 respectively.

When an exchange between various metal chelates MA_n and $M'B_{n'}$ takes place:

$$n'MA_n + nM'B_{n'} = n'MB_n + nM'A_{n'} \quad (8)$$

the following equation applies:

$$E_{MA_n-M'B_{n'}} = \frac{[MB_n]^{n'}[M'A_{n'}]^n}{[MA_n]^{n'}[M'B_{n'}]^n} = \frac{K^{n'}_{MB_n}K^n_{M'A_{n'}}}{K^{n'}_{MA_n}K^n_{M'B_{n'}}} = \frac{(E_{MA_n-HB})^{n'}}{(E_{M'A_{n'}-HB})^n} \quad (9)$$

From equation (9) it is evident that for quantitative transformation of chelate MA_n into MB_n (*i.e.*, for $[MB_n]/[MA_n] > 100$) the ratio

$$\frac{E_{MA_n-HB}}{(E_{M'A_{n'}-HB})^{n/n'}}\left(\frac{[M'B_{n'}]}{[M'A_{n'}]}\right)^{n/n'}$$

must be higher than 100. From the analysis of the expressions above it can be seen that it is more favourable to use as a reagent a chelate of a univalent metal than of a bi- or tervalent metal. However, the choice of the second chelating agent, HB, is even more important as its nature has a large influence on the value of E_{MA_n-HB}.

The equilibria considered above are valid only when mixed complexes are not being formed. If they are, their composition (and the corresponding equilibrium constants) can be found from the course of the chemical reaction, which can be generally written as:

$$MA_n + mHB = MA_{n-m}B_m + mHA. \quad (10)$$

Thus the corresponding exchange constant is given by

$$E_{MA_n-HB} = \frac{[MA_{n-m}B][HA]^m}{[MA_n][HB]^m}. \quad (11)$$

In the present paper an investigation of a mixed complex of arsenic with dithizone and diethyldithiocarbamic acid is given as an example.

EXPERIMENTAL

Apparatus

Spectrophotometer. Zeiss (Jena).
Recording spectrophotometer. Unicam S.P. 800.
Scintillation counter. Well-type with NaI(Tl) crystal.
pH-Meter. Radiometer pHM-2, Copenhagen.

Reagents

Unless otherwise stated, all reagents were of analytical reagent grade.

Carbon tetrachloride. Twice distilled, and after the second distillation stored not longer than one day. The quality of the carbon tetrachloride affects considerably the stability of solutions of diethyldithiocarbamic acid.

Dithizone, (H_2Dz). Purified by solvent extraction with carbon tetrachloride in the usual way.[1,2]

The concentration of dithizone solution is adjusted to the required value before each series of experiments by dilution with freshly distilled carbon tetrachloride, and checked spectrophotometrically at 620 mμ (molar absorptivity 32,800).[1,2]

Silver dithizonate, [*AgHDz*]. An excess of 0·1*M* silver nitrate (5 ml) in 50 ml of 0·05*M* sulphuric acid is extracted with 50 ml of $10^{-4}M$ dithizone in carbon tetrachloride. The organic layer is separated, filtered, diluted to the required concentration and stored protected from light. This solution must be freshly prepared before each series of experiments and its concentration checked spectrophotometrically at 462 mμ (molar absorptivity 30,500).[1,2]

Zinc dithizonate [$Zn(HDz)_2$]. To 50 ml of $2 \times 10^{-3}M$ zinc sulphate, 10 ml of 0·1*M* ammonia–ammonium chloride buffer (pH 8–9) are added and the extraction with 50 ml of $10^{-3}M$ dithizone solution is carried out. The organic layer is separated, washed with the same buffer solution, filtered and stored in a dark bottle. The concentration of zinc dithizonate is measured spectrophotometrically at 538 mμ (molar absorptivity 96,000).[2] This solution is fairly stable.

Sodium diethyldithiocarbamate ($NaDDC.2H_2O$). Sodium diethyldithiocarbamate dihydrate (22·5 mg) is dissolved in 100 ml of doubly distilled water, to which 0·1 g of ammonium carbonate is added. The concentration of this solution is checked by precipitation with an excess of copper sulphate. The copper diethyldithiocarbamate precipitated in this way from 0·50 ml of the reagent solution is extracted with 10 ml of carbon tetrachloride and its absorbance measured at 436 mμ (molar absorptivity 13,000).[2]

Diethyldithiocarbamic acid (*HDDC*). To 50 ml of $10^{-3}M$ solution of sodium diethyldithiocarbamate, placed in a separating funnel, 50 ml of carbon tetrachloride are added. Then between shakings, 0·5*M* sulphuric acid is added dropwise until the pH is 2–3. The organic layer is separated, filtered and stored protected from light. This solution is unstable and must be freshly prepared before each experiment. The concentration of diethyldithiocarbamic acid is determined by shaking the reagent with an excess of copper sulphate solution and measuring the absorbance as described above.

Silver diethyldithiocarbamate (*AgDDC*). To 50 ml of $10^{-3}M$ solution of sodium diethyldithiocarbamate 5 ml of $10^{-1}M$ silver nitrate are added and the acidity is adjusted to pH 2–3. The white precipitate formed is extracted with 50 ml of carbon tetrachloride, filtered and stored in a dark bottle.

Zinc diethyldithiocarbamate [$Zn(DDC)_2$]. Prepared in a similar way to silver diethyldithiocarbamate. Its concentration is determined spectrophotometrically after its conversion into copper diethyldithiocarbamate.

Arsenic diethyldithiocarbamate [$As(DDC)_3$]. Prepared and standardised in the same way as zinc diethyldithiocarbamate.

Sodium arsenite, 0·05 *M*. Prepared by dissolving 2·4725 g of arsenic trioxide in 20 ml of 1*M* sodium hydroxide and adding 0·5*M* sulphuric acid until the solution is either neutral or only slightly alkaline. The solution is transferred to a standard flask and made up to 500 ml.

Radioarsenic, ^{76}As. Prepared by irradiation of 1·0 mg of arsenic trioxide in a nuclear reactor with a flux of 1×10^{12} neutrons cm^{-2} sec^{-1} for 24 hr. After dissolution in 1*M* sodium hydroxide and dilution with water it is used for tracer experiments. The specific activity of radioarsenic prepared in this way is very high. For this reason the amount of isotopic carrier in solutions of ^{76}As is always negligible compared to the amount of arsenic in a non-active solution to be labelled.

RESULTS AND DISCUSSION

Investigation of exchange reaction between AgHDz and HDDC.

The experiments were carried out as follows. To a certain amount of silver dithizonate various known amounts of diethyldithiocarbamic acid were added. The volume was made up to 10 ml with carbon tetrachloride. After mixing, dithizone and silver diethyldithiocarbamate are immediately formed according to equation (1). For calculation of the exchange constant $E_{AgHDz-HDDC}$, it is necessary to determine the equilibrium concentrations of all species involved [see equation (4)]. The equilibrium concentration of dithizone and silver dithizonate can be found by the mixed colour method when the absorbancies at 620 mμ and 426 mμ are measured. The equilibrium concentration of silver diethyldithiocarbamate can be easily found from the difference between the original and equilibrium concentrations of silver dithizonate:

$$[AgDDC] = [AgHDz]_{orig} - [AgHDz] = [H_2Dz]. \qquad (12)$$

Similarly, the equilibrium concentration of diethyldithiocarbamic acid is calculated from the equation:

$$[HDDC] = [HDDC]_{orig} - [AgDDC] = [HDDC]_{orig} - [H_2Dz]. \quad (13)$$

However, because of the large value of the equilibrium constant $E_{AgHDz-HDDC}$ practically all the diethyldithiocarbamic acid reacts with silver dithizonate forming an equivalent amount of dithizone and therefore the precision of the determination of the *remaining* diethyldithiocarbamic acid is very low. For this reason it is necessary to add to the reacting species a known amount of silver diethyldithiocarbamate, so that reaction (1) is shifted to the left and sufficient diethyldithiocarbamic acid remains in the solution to enable a more precise determination of the equilibrium constant to be made. The results obtained are summarised in Table I.

TABLE I.—DETERMINATION OF EQUILIBRIUM CONSTANT $E_{AgHDz-HDDC}$.

Log of original concentrations				Log of equilibrium concentrations				Log
[AgHDz]	[HDDC]	[AgDDC]	[H_2Dz]	[AgHDz]	[HDDC]	[AgDDC]	[H_2Dz]	$E_{AgHDz-HDDC}$
−4·41	−4·51	−3·30		−4·92	−5·37	−3·28	−4·57	2·44
−4·41	−4·69	−3·30		−4·69	−5·69	−3·29	−4·74	2·35
−4·41	−4·42	−3·87		−5·30	−5·48	−3·88	−4·45	2·45
−4·40	−4·42	−3·87		−5·35	−5·62	−3·88	−4·45	2·64
−4·40	−4·58	−3·87		−4·84	−6·40	−3·90	−4·59	2·50
		−3·30	−4·56	−5·32	−5·32	−3·31	−4·64	2·69
		−3·30	−4·68	−5·39	−5·39	−3·31	−4·78	2·69
		−3·30	−4·81	−5·48	−5·48	−3·31	−4·95	2·70
		−3·30	−4·90	−5·47	−5·47	−3·31	−5·04	2·59
		−3·30	−4·98	−5·55	−5·55	−3·31	−5·13	2·66
		−3·60	−4·81	−5·60	−5·60	−3·61	−4·87	2·72
		−3·60	−4·98	−5·60	−5·60	−3·61	−5·06	2·53
		−4·00	−4·65	−5·72	−5·72	−4·01	−4·68	2·75
		−4·30	−4·54	−5·70	−5·70	−4·32	−4·57	2·51
		−4·52	−4·54	−5·83	−5·83	−4·54	−4·57	2·55
							Average =	2·58 ± 0·03

The equilibrium constant $E_{AgHDz-HDDC}$ can also be measured by investigation of the exchange reaction of the products, *i.e.*, by mixing silver diethyldithiocarbamate and dithizone. The equilibrium concentrations of silver dithizonate and dithizone are determined by the mixed colour method, and of silver diethyldithiocarbamate and diethyldithiocarbamic acid by calculation from the relationships

$$[AgDDC] = [AgDDC]_{orig} - [AgHDz] \quad (14)$$

$$[HDDC] = [AgDDC]_{orig} - [AgDDC] = [AgHDz]. \quad (15)$$

The results obtained in this way are in good agreement with those obtained by the investigation of the reverse reaction (see Table I).

The mean value of log $E_{AgHDz-HDDC}$ is 2·58 ± 0·03. If the log of the extraction constant of silver dithizonate is taken to be 8·94,[2] the log of the extraction constant of silver diethyldithiocarbamate according to equation (4) is 8·94 + 2·58 = 11·52 (solvent carbon tetrachloride). It is interesting to note that the value of the log of this constant calculated from Still's data[3] is 12 (chloroform as solvent).

Table II.—DETERMINATION OF EQUILIBRIUM CONSTANT $E_{Zn(HDz)_2-HDDC}$

Log of original concentrations				Log of equilibrium concentrations				
$[Zn(HDz)_2]$	[HDDC]	$[Zn(DDC)_2]$	$[H_2Dz]$	$[Zn(HDz)_2]$	[HDDC]	$[Zn(DDC)_2]$	$[H_2Dz]$	Log $E_{Zn(HDz)_2-HDDC}$
−4·79	−5·00			−5·29	−5·42	−5·51	−5·21	0·20
−4·79	−4·79			−5·49	−5·07	−5·30	−5·00	0·33
−5·05	−5·21			−5·17	−5·78	−5·65	−5·36	0·37
−5·05	−5·09			−5·20	−5·56	−5·57	−5·26	0·23
−5·05	−4·91			−5·30	−5·35	−5·41	−5·11	0·37
−5·05	−4·84			−5·32	−5·24	−5·37	−5·07	0·29
−5·05	−4·78			−5·36	−5·14	−5·34	−5·04	0·22
−5·05	−4·73			−5·39	−5·06	−5·31	−5·01	0·18
−5·05	−4·59			−5·42	−4·99	−5·29	−4·99	0·18
−5·05	−4·41			−5·78	−4·61	−5·15	−4·85	0·15
		−4·00	−4·64	−5·08	−4·78	−4·04	−5·25	0·10
		−4·05	−4·65	−5·07	−4·77	−4·07	−5·21	0·12
		−4·05	−4·57	−5·01	−4·71	−4·09	−5·11	0·12
		−4·11	−4·70	−5·15	−4·84	−4·16	−5·26	0·15
		−4·17	−4·70	−5·14	−4·84	−4·22	−5·22	0·16
		−4·30	−4·81	−5·27	−4·97	−4·34	−5·37	0·13
		−4·30	−4·52	−5·08	−4·78	−4·34	−4·91	0·44
		−4·37	−4·85	−5·34	−5·04	−4·54	−5·31	0·26
		−4·41	−4·85	−5·34	−5·04	−4·47	−5·34	0·27
		−4·47	−4·79	−5·23	−4·93	−4·55	−5·06	0·42
								Average = 0·24 ± 0·03

Investigation of exchange reaction between ZnHDz and HDDC

This investigation was carried out in a way similar to that described for silver. Equilibrium concentrations of zinc dithizonate and dithizone were determined by the mixed colour method from the absorbances measured at 538 mμ and 620 mμ; equilibrium concentrations of zinc diethyldithiocarbamate and diethyldithiocarbamic acid were calculated from

$$[Zn(DDC)_2] = [Zn(HDz)_2]_{orig} - [Zn(HDz)] = 0{\cdot}5[H_2Dz] \quad (16)$$

$$[HDDC] = [HDDC]_{orig} - 2[Zn(DDC)_2] = [HDDC]_{orig} - [H_2Dz]. \quad (17)$$

The reversibility of this reaction has been studied by mixing zinc diethyldithiocarbamate with dithizone. The rate of this reaction is very high; equilibrium is reached in

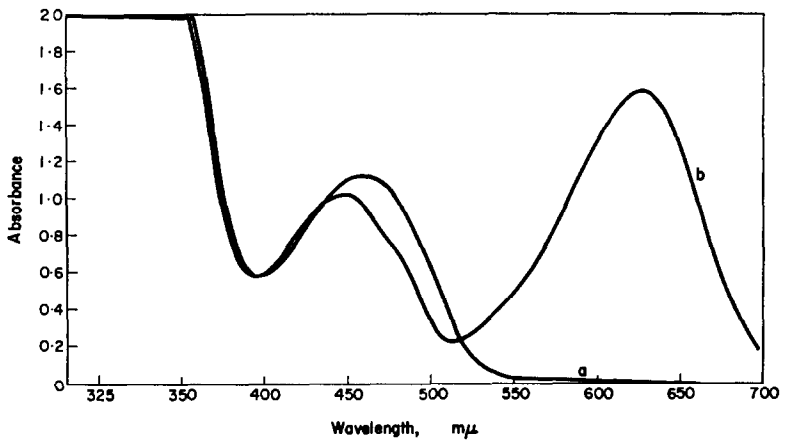

FIG. 1.—Absorption spectra of arsenic dithizonate–diethyldithiocarbamate (AsDzDDC) and of dithizone (H_2Dz) liberated from this complex.
Path-length, 1·00 cm; carbon tetrachloride used as solvent and reference sample.
Curve *a*—AsDzDDC, curve *b*—H_2Dz.

a few seconds. From the results summarised in Table II it can be seen that reaction (2) is fully reversible, for the values of the exchange constant do not depend on the way in which the equilibrium has been reached.

The mean value of log $E_{Zn(HDz)_2-HDDC}$ is 0·24 ± 0·03, so the log of the extraction constant of zinc diethyldithiocarbamate is 2·54 (assuming that log $K_{Zn(HDz)_2} = 2{\cdot}3$).[2] The value of log $K_{Zn(DDC)_2}$ determined by solvent extraction is 2·95.[4]

Investigation of exchange reaction between As(DDC)$_3$ and H_2Dz

The examples above deal with the investigation of metal dithizonates and diethyldithiocarbamates of which the properties are known. However, it is interesting to investigate an exchange reaction the products of which might include a complex not previously described. We have investigated a reaction between arsenic diethyldithiocarbamate and dithizone in carbon tetrachloride. It has been observed that a yellow complex is formed as a result of this reaction. The spectrum of this complex was measured after the excess of dithizone had been removed by washing with ammonia–ammonium chloride buffer, pH ~ 9·5 (Fig. 1, Curve a). It differs from the spectra

of all known dithizonates and decomposition products of dithizone. The complex is fairly stable and can be stored for several days. It was also found that Beer's law is obeyed over the range 0–5 $\times$ $10^{-5}M$ (at 460 mμ).

Further, the behaviour of this complex, when shaken with an aqueous phase, has been studied spectrophotometrically at 400 mμ (Fig. 2). At pH lower than 4·5 the complex is destroyed and the green colour of liberated dithizone appears (Fig. 1,

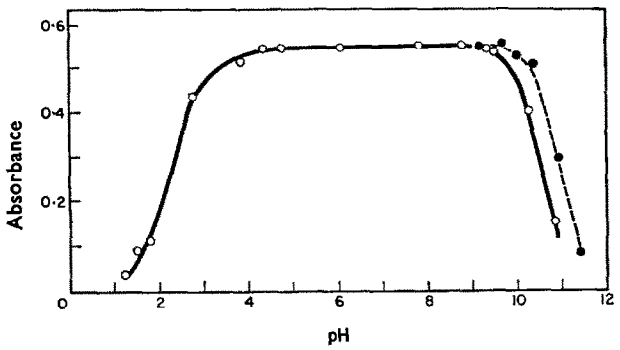

FIG. 2.—Decomposition of 2·5 $\times$ $10^{-5}M$ AsDzDDC when shaken with an aqueous solution at various pH values.
Time of shaking: 2 min (full line), 15 sec (dotted line). At pH > 7; 1 ml of 0·05M KCN present.

curve b). The complex can also be destroyed by hydrogen sulphide (yellow As_2S_3 is precipitated) or by an excess of diethyldithiocarbamic acid in carbon tetrachloride. These observations have been verified by means of radioarsenic as a tracer.

From the amount of arsenic originally present in the yellow complex (determined by measuring its radioactivity) and from the amount of dithizone liberated by shaking with 1M sulphuric acid it has been found that the ratio between arsenic and dithizone is 1:1.

From these experiments it follows that the composition of the complex formed is either As(HDz)$(DDC)_2$ or AsDzDDC. However, if a primary dithizonate [such as Ag(HDz), In$(HDz)_3$, *etc.*] is added to arsenic diethyldithiocarbamate, free dithizone is always liberated, which can only be explained by the formation of a complex AsDzDDC.

To check this statement the reaction

$$As(DDC)_3 + H_2Dz = AsDzDDC + 2HDDC \qquad (18)$$

was investigated and the value of the exchange constant

$$E_{As(DDC)_3-H_2Dz} = \frac{[AsDzDDC][HDDC]^2}{[As(DDC)_3][H_2Dz]} \qquad (19)$$

has been calculated. In this case, the equilibrium concentration of dithizone was spectrophotometrically determined at 620 mμ. Other equilibrium concentrations of species involved were determined from the original concentrations of arsenic

diethyldithiocarbamate and dithizone according to the equations

$$[\text{AsDzDDC}] = [\text{H}_2\text{Dz}]_{\text{orig}} - [\text{H}_2\text{Dz}] \tag{20}$$

$$[\text{HDDC}] = 2[\text{AsDzDDC}] \tag{21}$$

$$[\text{As(DDC)}_3] = [\text{As(DDC)}_3]_{\text{orig}} - [\text{AsDzDDC}]. \tag{22}$$

It was found that it takes 2–4 min to reach equilibrium, after mixing of arsenic diethyldithiocarbamate and dithizone.

From Table III, it can be seen that $\log E_{\text{As(DDC)}_3\text{–H}_2\text{Dz}}$ is $-7{\cdot}93 \pm 0{\cdot}06$. This value is not as precise as the values for $\log E_{\text{AgHDz–HDDC}}$ and $\log E_{\text{Zn(HDz)}_2\text{–HDDC}}$

TABLE III.—DETERMINATION OF EQUILIBRIUM CONSTANT $E_{\text{As(DDC)}_3\text{–H}_2\text{Dz}}$

Log of original concentration		Log of equilibrium concentrations				Log
[As(DDC)$_3$]	[H$_2$Dz]	[As(DDC)$_3$]	[H$_2$Dz]	[AsDzDDC]	[HDDC]	$E_{\text{As(DDC)}_3\text{–H}_2\text{Dz}}$
−4·78	−4·76	−4·81	−4·78	−6·05	−5·75	−7·96
−4·48	−4·76	−4·50	−4·79	−5·89	−5·59	−7·78
−4·18	−4·82	−4·19	−4·87	−5·85	−5·55	−7·89
−4·00	−4·82	−4·01	−4·88	−5·72	−5·42	−7·67
−4·00	−4·76	−4·01	−4·81	−5·73	−5·43	−7·77
−3·88	−4·89	−3·89	−4·96	−5·72	−5·42	−7·71
−3·78	−5·21	−3·78	−5·30	−5·93	−5·63	−8·11
−3·78	−4·89	−3·79	−4·94	−5·82	−5·52	−8·13
−3·78	−4·77	−3·78	−4·81	−5·80	−5·50	−8·21
−3·78	−4·67	−3·78	−4·81	−5·74	−5·44	−8·03
					Average =	$-7{\cdot}93 \pm 0{\cdot}06$

because during the time of equilibration some diethyldithiocarbamic acid may be decomposed. To confirm the value of this constant, the exchange reaction

$$\text{As(DDC)}_3 + 2\text{AgHDz} = \text{AsDzDDC} + 2\text{AgDDC} + \text{H}_2\text{Dz} \tag{23}$$

was studied to determine the value of

$$E_{\text{As(DDC)}_3\text{–AgHDz}} = \frac{[\text{AsDzDDC}][\text{AgDDC}]^2[\text{H}_2\text{Dz}]}{[\text{As(DDC)}_3][\text{AgHDz}]^2}. \tag{24}$$

This equilibrium is also reached in 2–4 min from mixing of the reactants. From the concentration of dithizone liberated the equilibrium concentrations of other species involved can be calculated as follows:

$$[\text{AsDzDDC}] = [\text{H}_2\text{Dz}] \tag{25}$$

$$[\text{AgDDC}] = 2[\text{H}_2\text{Dz}] \tag{26}$$

$$[\text{As(DDC)}_3] = [\text{As(DDC)}_3]_{\text{orig}} - [\text{AsDzDDC}] \tag{27}$$

$$[\text{AgHDz}] = [\text{AgHDz}]_{\text{orig}} - [\text{AgDDC}]. \tag{28}$$

The mean value of $\log E_{As(DDC)_3-AgHDz}$ is $-2{\cdot}97 \pm 0{\cdot}03$ (see Table IV). From equations (4), (19) and (24) it can be seen that

$$\log E_{As(DDC)_3-AgHDz} = 2 \log E_{AgHDz-HDDC} + \log E_{As(DDC)_3-H_2Dz}$$

$$= 5{\cdot}16 - 7{\cdot}93 = -2{\cdot}77$$

which is in very good agreement with the value $-2{\cdot}97$ found from the reaction of arsenic diethyldithiocarbamate and dithizone.

TABLE IV.—DETERMINATION OF EQUILIBRIUM CONSTANT $E_{As(DDC)_3-AgHDz}$

Log of original concentrations		Log of equilibrium concentrations					
[As(DDC)$_3$]	[AgHDz]	[As(DDC)$_3$]	[AgHDz]	[AsDzDDC]	[AgDDC]	[H$_2$Dz]	Log $E_{As(DDC)_3-AgHDz}$
−4·70	−4·59	−5·07	−5·60	−4·94	−4·64	−4·94	−2·89
−4·58	−4·59	−4·83	−5·62	−4·94	−4·64	−4·94	−3·09
−4·48	−4·59	−4·67	−5·68	−4·93	−4·63	−4·93	−3·09
−4·48	−4·42	−4·80	−5·40	−4·77	−4·47	−4·77	−2·88
−4·48	−4·32	−4·89	−5·13	−4·70	−4·40	−4·70	−3·05
−4·48	−4·24	−5·01	−4·97	−4·63	−4·33	−4·63	−3·07
−4·48	−4·18	−5·15	−4·84	−4·58	−4·28	−4·58	−2·89
−4·48	−4·12	−5·30	−4·70	−4·55	−4·25	−4·55	−2·90
−4·40	−4·59	−4·55	−5·82	−4·92	−4·62	−4·92	−2·89
−4·34	−4·59	−4·47	−5·82	−4·92	−4·62	−4·92	−2·97
						Average =	$-2{\cdot}97 \pm 0{\cdot}03$

Spectrophotometric determination of small amounts of arsenic

These experiments suggest a method for the spectrophotometric determination of arsenic. The value of $E_{As(DDC)_3-AgHDz}$ is such that arsenic diethyldithiocarbamate is quantitatively transformed into the complex AsDzDDC even when only a tenfold excess of silver dithizonate is used. Obviously two possibilities exist for the determination of arsenic in this way [equation (23)]: (1) measurement of the absorbance of the complex AsDzDDC at 450 mμ, (2) measurement of the absorbance of dithizone liberated at 620 mμ. When the absorbance of AsDzDDC is measured the excess of silver dithizonate as well as the dithizone liberated must be removed. For this reason the second approach was chosen. The principle is very simple: arsenic(III) is quantitatively extracted as diethyldithiocarbamate at a pH lower than 5,[5] and then allowed to react with silver dithizonate with the quantitative release of dithizone [equations (1) and (23)]. At pH lower than 2–3, diethyldithiocarbamic acid in the aqueous phase, which would also displace dithizon, is immediately destroyed, whilst arsenic diethyldithiocarbamate is unaffected. To increase the selectivity, metals forming extractable diethyldithiocarbamates or dithizonates could be removed by a preliminary extraction at pH > 8, at which arsenic(III) is not extracted.

Procedure

Place a neutral or slightly acid solution (volume 10–20 ml), containing the arsenic(III) to be determined (0–40 μg As) in a 50 ml separating funnel. Add 1 ml of 0·1*M* ammonium acetate followed by 1 ml of $4 \times 10^{-3}M$ sodium diethyldithiocarbamate solution. Shake for a few sec, then add 5 ml of 0·1*N* sulphuric acid and shake again. Allow to stand for 60 sec (to destroy excess of diethyldithiocarbamic acid) then add 10·0 ml of carbon tetrachloride and extract for 3 min. To a suitable aliquot of extract (6·00 ml) add 4·00 ml of freshly prepared silver dithizonate ($2 \times 10^{-4}M$) in carbon tetrachloride. Measure the amount of dithizone liberated, at 620 mμ. The colour is developed after 3 min and is stable for at least 10 min.

Theoretically 1 μg of arsenic liberates $1{\cdot}4 \times 10^{-6}$ mole of dithizone the absorbance of which in a 1·00 cm cell is 0·460 (volume 1 ml). However, in practice a suitable aliquot of organic layer must be taken and further diluted with colour forming reagent (silver dithizonate), and it is preferable to use a calibration curve

CONCLUSION

A study of exchange equilibria between metal dithizonates and diethyldithiocarbamates has been made to show that such exchanges take place and that they can be explained. Generally the rates of reaching equilibrium are very high, probably because of the lack of solvolysis and solvation in the non-polar organic solvents used. Very good experimental reproducibility has been observed in all cases.

These properties are valuable analytically and an attempt has been made to show the potentialities of the method; a procedure for the spectrophotometric determination of small amounts of arsenic has been proposed. Its sensitivity is high, and to judge from the known properties of metal dithizonates and diethyldithiocarbamates[2] it is likely to be highly selective. Investigations to assess its practical worth are under way.

In the present study an exchange between metal chelates with the same functional groups (—SH) is described, but exchange between chelates containing different functional groups (*e.g.*, dithizonates—cupferrates) will be probably more valuable analytically, and will also be investigated in our laboratory. It is hoped that exchange of chelates in the organic phase will contribute not only to the study of solvent extraction and composition of metal chelates but also to development of selective spectrophotometric and titrimetric procedures.

Zusammenfassung—Durch organische Lösungsmittel aus wäßriger Phase extrahierte Metallchelate können mit in dem selben Lösungsmittel gelösten anderen Chelatbildnern (oder deren Metallchelaten) reagieren. Dieser Austausch von Metallchelaten in organischer Phase kann verwendet werden (1) zur Ermittlung der Lage des Austauschgleichgewichts und der Zusammensetzung der geblideten Metallchelate; (2) zur Bestimmung von Extraktionskonstanten; (3) zur Darstellung neuer in organischen Lösungsmitteln löslicher Inner-Komplexe; (4) zur spektrophotometrischen Bestimmung kleiner Metallmengen. Theorie und experimentelle Realisierung des Phänomens werden mitgeteilt. Die Extraktionskonstanten der Diäthyldithiocarbamate von Silber und Zink in Tetrachlorkohlenstoff wurden über die Extraktionskonstanten der Dithizonate bestimmt. Ein gemischter Komplex von Arsen(III) mit Dithizon und Diäthyldithiocarbaminsäure wurde dargestellt und seine Eigenschaften untersucht. Eine einfache Methode zur spektrophotometrischen Bestimmung von Mikrogrammengen Arsen wird vorgeschlagen.

Résumé—Des chélates métalliques, extraits d'une phase aqueuse par des solvants organiques, peuvent réagir avec d'autres agents chélatants (ou leurs chélates métalliques) dissous dans le même solvant. Cet échange de chélates métalliques dans la phase organique peut être utilisé pour (1) l'étude de l'équilibre d'échange et de la composition des

chélates métalliques formés, (2) la détermination des constantes d'extraction, (3) la préparation de nouveaux complexes internes solubles en solvants organiques et (4) le dosage spectrophotométrique de petites quantités de métaux. On donne la théorie et la vérification expérimentale de ce phénomène. On a déterminé les constantes d'extraction des diéthyldithiocarbamates d'argent et de zinc en tétrachlorure de carbone au moyen des constantes d'extraction des dithizonates correspondants. On a préparé un complexe mixte d'arsenic(III) avec la dithizone et l'acide diéthyldithiocarbamique et étudié ses propriétes. On propose une méthode simple pour le dosage spectrophotométrique de quantités d'arsenic de l'ordre du microgramme.

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SPECTROPHOTOMETRIC DETERMINATION OF HEXAFLUOROARSENATE WITH FERROIN

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Summary—A spectrophotometric method for the hexafluoroarsenate anion is described. The determination involves selective extraction of the tris(1,10-phenanthroline)iron(II) salt of the anion into n-butyronitrile, followed by measurement of the absorbance of the organic layer. The extracts give good Beer's law plots over a wide range of concentrations and more than 98% of the hexafluoroarsenate is removed in a single extraction. Interference studies were made on a number of anions.

HEXAFLUOROARSENATE is one anion for which very few analytical methods have been developed. Lange and Müller[1] erroneously thought they had synthesized this anion and indicated that it could be precipitated as nitron (4,5-dihydro-1,4-diphenyl-3,5-phenylimino-1,2,4-triazole) hexafluoroarsenate monohydrate. In the process of a study of complex fluoroarsenates, Dess and Parry[2] showed that the actual anionic species produced by Lange and Müller was the $[AsF_5OH^-]$ ion and that nitron precipitated this anion as the unhydrated salt. These investigators also produced the hexafluoroarsenate ion and found that it was quite hydrolytically stable, in contrast to the $[AsF_5OH^-]$ anion. Dess[3] established that the hexafluoroarsenate ion was precipitated by nitron or tetraphenylarsonium chloride and that the corresponding salts were both useful for gravimetric determinations. He found, however, that the physical properties of the tetraphenylarsonium salt were more suitable for analytical application, and developed a gravimetric method for hexafluoroarsenate, utilizing tetraphenylarsonium chloride. This method appeared to give good results and is so far the only fully developed analytical method for this anion.

Ferroin [tris(1,10-phenanthroline)iron(II)sulphate] has been used previously as a spectrophotometric reagent for the determination of perchlorate[4] and hexafluorophosphate.[5] The present spectrophotometric method for hexafluoroarsenate is similar to the method for hexafluorophosphate. It entails the extraction of tris(1,10-phenanthroline)iron(II) hexafluoroarsenate with n-butyronitrile followed by measurement of the absorbance of the organic layer as a function of the amount of hexafluoroarsenate present in the aqueous layer.

EXPERIMENTAL

Reagents

A 0·01*M* solution of ferroin was prepared from iron(II) sulphate and 1,10-phenanthroline. A standard solution of $2{\cdot}784 \times 10^{-3}M$ potassium hexafluoroarsenate was prepared from $KAsF_6$ previously analysed by precipitation with tetraphenylarsonium chloride according to a procedure developed in this laboratory. Tetraphenylarsonium chloride was obtained from the G. F. Smith Chemical Co. of Columbus, Ohio. n-Butyronitrile was obtained from Eastman Organic Chemicals and was used without purification.

Procedure for calibration curve

Portions of 0·200–2·000 ml of the hexafluoroarsenate solution were added to 15-ml glass-stoppered centrifuge tubes and diluted with water to 2·000 ml. Then 1 ml of ferroin solution and 5·000 ml of n-butyronitrile were added to each, and the mixtures were shaken vigorously for 2 min and then centrifuged for 2 min to separate the layers. A 1-ml aliquot of each upper (organic) layer was taken and diluted to volume with n-butyronitrile in a 5-ml volumetric flask. The transmittance of this solution was measured immediately in a 1-cm cell against pure n-butyronitrile at 505 mμ on a Beckman DU spectrophotometer with a 0·1-mm slit-width. The transmittances were converted into absorbances which were tabulated and plotted *vs.* mmoles of potassium hexafluoroarsenate present. Unknowns may be determined by applying a similar procedure and reading off the concentration from the calibration curve. In the presence of mild interferences, the standard plot should be run with amounts of the interfering ions equal to those present in the unknown solution, or the method of standard additions could be used.

Development of method

Standardisation of the potassium hexafluoroarsenate. Take 10 ml of a solution containing from 0·04 to 0·06 g of the salt, add 10 ml of water and 1 ml of 5*M* ammonium chloride. Slowly add, with stirring, 5 ml of 0·09*M* tetraphenylarsonium chloride. Heat on a hot-plate until the precipitate flocculates. Cool to room temperature, filter off on a sintered glass crucible, and wash with 40–50 ml of 0·001*M* hydrochloric acid. Dry to constant weight at 105° and weigh as $(C_6H_5)_4As_3F_6$.

Effect of pH. The effect of pH on the extraction was determined by performing the extraction of the hexafluoroarsenate anion from a series of aqueous solutions buffered in the range pH 2·2–10·6.

Anion interference studies. A series of anions was tested for possible interference with the experimental method by adding 1 ml of 0·20*M* solution of a sodium, potassium or ammonium salt of the anion to 1 ml of $2·784 \times 10^{-3}$*M* hexafluoroarsenate and applying the extraction procedure. Fluoride, which did not interfere when present in the amount stated, was tested for interference at higher concentrations.

Stability studies on the extracts. Extractions were made on a series of hexafluoroarsenate solutions in the usual way, after which the absorbances were measured as a function of time over a 24-hr period.

Exhaustive extractions. Two ml of hexafluoroarsenate solution mixed with 1 ml of ferroin were extracted with four successive 5·00-ml portions of n-butyronitrile. The organic extracts were combined and diluted to volume with n-butyronitrile in a 25-ml volumetric flask, and the absorbance of this solution was measured.

RESULTS AND DISCUSSION

Data from the gravimetric standardisation of the hexafluoroarsenate with tetraphenylarsonium chloride are given in Table I. The relative precision of the method is shown because this information has not previously appeared in the literature.

TABLE I.—GRAVIMETRIC STANDARDISATION OF THE $KAsF_6$ SAMPLE WITH TETRAPHENYLARSONIUM CHLORIDE

$KAsF_6$ taken, *g*	No. of determinations	Mean $(C_6H_5)_4AsAsF_6$, *g*	Mean AsF_6^-, %	Relative standard deviation, %
0·04604	3	0·1157	$82·9_0$	$0·5_2$
0·04656	3	0·1168	$82·8_1$	$0·3_4$
0·04270	3	0·1074	$83·0_3$	$0·3_7$
0·03917	3	0·0983	$82·8_5$	$0·2_0$
0·05218	3	0·1311	$82·9_4$	$0·0_8$
0·04158	3	0·1045	$82·9_7$	$0·1_9$

Overall mean AsF_6^- = 82·93%; theoretical AsF_6^- in $KAsF_6$ = 82·85%.

It was found that the spectrophotometric method gives good Beer's law plots over the range of hexafluoroarsenate concentrations used. Based on a least-squares analysis of the data, the slope of the calibration line was found to be 229 $mmole^{-1}.\ cm^{-1}$ with a standard deviation of 1·44 $mmole^{-1}.cm^{-1}$. It was found from the exhaustive extractions (see Table II) that a single extraction removes approximately 98% of the hexafluoroarsenate from the aqueous layer. The rate of fading of the colour is also shown

TABLE II.—ABSORBANCES OBTAINED FOR SINGLE EXTRACTION, EXHAUSTIVE EXTRACTION, AND STABILITY STUDY ON EXTRACTS

$KAsF_6$ μmole	Absorbances					
	Single extraction*	Exhaustive extraction*	Measured after			
			2 hr	5 hr	10 hr	24 hr
0·5568	—	0·138	—	—	—	—
1·392	0·315	0·335	0·285	0·267	0·249	0·245
2·227	0·524	0·526	0·494	0·489	0·469	—
2·784	0·607	0·635	0·585	0·572	0·554	0·553
3·341	0·769	—	0·740	0·724	0·702	0·697
3·619	—	0·860	—	—	—	—
4·176	0·963	0·962	0·929	0·915	0·894	0·903
5·011	1·15	1·17	1·12	1·11	1·10	1·09
5·568	1·28	1·30	1·25	1·23	1·22	1·21

* The dilution factors are the same, so the absorbances are directly comparable.

TABLE III.—ANION INTERFERENCES

Compound used	Effect
Ammonium acetate	negative
Sodium carbonate	negative
Ammonium chloride	negative
Potassium chromate	negative
Sodium dihydrogen phosphate	lowered absorbance slightly
Potassium ferricyanide	lowered absorbance slightly
Potassium fluoride	negative
Sodium hydrogen phosphate	negative
Potassium iodate	negative
Sodium monofluorophosphate	negative
Sodium phosphate	very slight extraction
Sodium sulphate	negative
Sodium sulphite	negative
Sodium potassium tartrate	negative
Sodium oxalate	negative

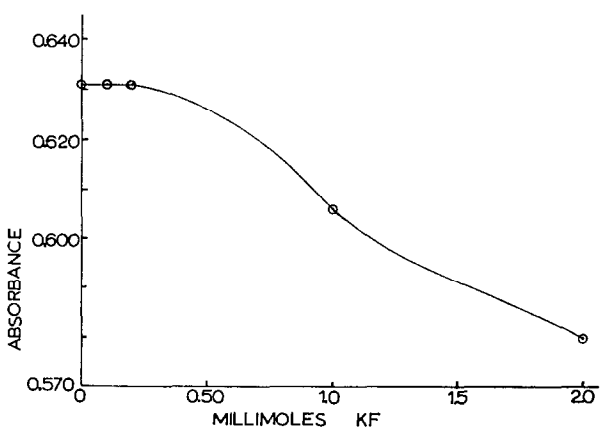

FIG. 1.—Effect of KF on the spectrophotometric method.

in Table II. From these results it would seem imperative that the extractions and measurements be made over a short period of time. It was found that pH variations between 2·2 and 10·6 had essentially no effect on the results. Data from the anion interference study are shown in Table III. As can be seen from Fig. 1, fluoride does not interfere until present in amounts greater than 0·20 mmoles.

This amount compares favourably with other spectrophotometric methods in terms of sensitivity, reproducibility and adherence to Beer's law. This method using potassium hexafluoroarsenate, standardised by the given gravimetric method, as a secondary standard, should prove to be a very reliable and fast method for routine analyses of hexafluoroarsenate.

Acknowledgement—The potassium hexafluoroarsenate used in this work was donated by the Ozark-Mahoning Co., Tulsa, Oklahoma, U.S.A.

Zusammenfassung—Eine spektrophotometrische Methode zur Bestimmung des Hexafluoroarsenat-Anions wird beschrieben. Bei dem Verfahren wird das Tris(1,10-phenanthrolin)eisen(II)- Salz des Anions in *n*-Butyronitril extrahiert und die Extinktion der organischen Schicht gemessen. Die Extrakte geben gut lineare Extinktions-Konzentrations-diagramme in einem weiten Konzentrationsbereich und mehr als 98% des Hexafluoroarsenats werden bei einer Extraktion erfaßt. Störuntersuchungen wurden en einer Anzahl von Anionen gemacht.

Résumé—On décrit une méthode spectrophotométrique pour l'anion hexafluoroarséniate. Le dosage comprend une extraction sélective du sel tris(1,10-phénanthroline) fer(II) de l'anion en *n*-butyronitrile, suivie de la mesure de l'absorption de la couche organique. Les extraits donnent des tracés suivant bien la loi de Beer dans un large domaine de concentrations, et l'on extrait plus de 98% de l'hexafluoroarséniate en une seule extraction. Des études d'interférence ont été effectuées pour un certain nombre d'anions.

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POLAROGRAPHIC STUDY OF INHIBITORS AND CATALYSTS FOR THE REACTION OF DISSOLVED OXYGEN WITH SULPHITE ION

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Summary—Oxygen reduction waves are utilized to determine the inhibition effect of some reagents commonly added in polarographic work, on the reaction of dissolved oxygen with sodium sulphite in neutral and alkaline supporting electrolytes. Alkali metal hydroxides, EDTA, TEA, ethanol and methyl cellosolve inhibited the reaction to various extents. In this work, it appeared that some metallic ions, such as cobalt(II) and manganese(II) can catalyse the oxygen–sulphite reaction, enabling wider application to be made of sodium sulphite for de-oxygenation of neutral and alkaline supporting electrolytes containing inhibitors.

DISSOLVED oxygen gives two reduction waves at the dropping mercury electrode. The first corresponds to the reduction of oxygen to hydrogen peroxide and the second to its reduction to water or hydroxyl ion. Inert gas, *i.e.*, nitrogen, hydrogen or helium, is bubbled into solutions to displace dissolved oxygen and eliminate its interference in polarographic determinations. Sodium sulphite has found use in routine polarographic determinations, by virtue of its ability to remove dissolved oxygen from neutral and alkaline supporting electrolytes. When theoretical studies are involved, the use of sodium sulphite is undesirable, mainly because of its formation of metallic complexes and its reactivity towards some organic compounds. Its limited use in routine analysis stems, however, from the slow rate of absorption of oxygen under the influence of inhibitors.

Lingane[1] has reported that the oxygen–sulphite reaction is so slow in sodium hydroxide solutions containing plumbite ion, that sulphite ion cannot be used to remove dissolved oxygen. Israel and Vromen[2] observed in the course of determination of silver(I) that potassium cyanide in copper-free ammoniacal solution depolarized the dropping mercury electrode in the presence of sodium sulphite. They recommended the addition of 0·1 g of copper ion to each l. of solution, while keeping cyanide present in excess, to obviate this interference. Meites[3] and Stackelberg[4] emphasized the catalytic effect of copper ion on the oxygen–sulphite reaction. Zuman[5] did not recommend the use of sodium sulphite for de-aeration of solutions in organic polarographic determinations since sulphite is reactive towards many organic compounds and may interfere in their determination. Stackelberg[4] mentioned that organic compounds often slow down the rate of the oxygen–sulphite reaction. In organic determinations such as of azobenzene and dipicrylamine[6], sodium sulphite was not suitable because it tended to react slowly with dissolved oxygen in the presence of organic constituents. This became evident when catalysts were introduced.

The present work demonstrates the use of oxygen reduction waves at the dropping mercury electrode for the rapid study of the effect of various inhibitors and catalysts on the oxygen–sulphite reaction. The inhibitors chosen were those commonly used in polarographic determinations, such as triethanolamine (TEA), EDTA, ethanol and alkali hydroxides. The catalysts were ions that interfere the least in polarographic determinations, such as cobalt(II) and manganese(II). For this reason other known metallic oxygen-carriers, such as iron(II) and copper(II), were not included in this work in spite of their evident effectiveness in catalysing the oxygen–sulphite reaction. Although the knowledge obtained in this study, and in the chronoamperometric study that follows,[7] is particularly applicable to polarography, it may be used for the broader aspects of this reaction in commercial processes, where either inhibition or catalysis of reactions may be desirable.[8]

EXPERIMENTAL

Apparatus

A Radiometer type PO4 recording polarograph was used, with the cell supplied. A separate saturated calomel electrode was connected to the main cell compartment by an agar-saturated potassium chloride bridge. When necessary, deoxygenation was effected by bubbling nitrogen into the solution through a capillary which could be raised during measurements. For more efficient de-oxygenation with nitrogen, a modified H-cell with fritted glass cylinder[9] was employed.

Reagents

Analytical grade reagents were used. High purity nitrogen was freed from traces of oxygen by passage through a solution of chromium(II) in dilute sulphuric acid containing an excess of amalgamated zinc. Mercury was cleaned by "pin-holing" (passing it through a pin-hole in a filter paper) and by bubbling air through it for a few days after covering it with 10% nitric acid, followed by washing, degreasing, pin-holing and drying.[10]

The following reagent solutions were prepared: (1) cobalt(II) nitrate solution: 5·0 g/l; (2) manganese(II) sulphate: 5·2 g/l; (3) sodium sulphite: 250 g/l, freshly prepared every week; (4) sodium hydroxide: 2*F*; (5) ammonium hydroxide–ammonium chloride: 2*F* in each; (6) potassium chloride: 2*F*. Triethanolamine (TEA) and the disodium salt of ethylenediaminetetra-acetic acid (EDTA), were added by weighing the required amounts.

RESULTS AND CONCLUSIONS

Polarograms of 1*F* ammonia–ammonium chloride supporting electrolyte, obtained after de-oxygenation with sodium sulphite or by bubbling purified nitrogen, indicated that sodium sulphite was efficient in eliminating dissolved oxygen. Current measurements, at the plateau of the first oxygen reduction wave, −0·3 V *vs.* S.C.E., were lowest, *ca.* 0·032 μA (anodic), when solutions containing 26 g of sodium sulphite per l. were examined. After prolonged bubbling of purified nitrogen through the supporting electrolyte in the modified H-cell with a fritted glass cylinder, the anodic current obtained was *ca.* 0·011 μA. Less efficient de-oxygenation was obtained when a capillary was used for bubbling nitrogen.

Polarogram *a* in Fig. 1, depicts oxygen reduction waves in 1*F* sodium hydroxide supporting electrolyte. The addition of 25 g of sodium sulphite per l. to the same supporting electrolyte did not eliminate the reaction waves of dissolved oxygen (polarogram *b* Fig. 1). The first reduction wave decreased, which is an indication of partial de-oxygenation. The dip that occurs at *ca.* −1·0 V *vs.* S.C.E., is a familiar phenomenon,[11] resulting from partial blocking of the surface of the electrode by adsorptive constituents and, depending on the extent of coverage, renders the electrode surface unavailable for the reduction of active depolarizers (oxygen in this instance).

At a more negative potential, desorption follows, the dip disappears and the whole surface becomes available for reduction, and therefore the plateau of the second wave of polarogram *b* represents the normal sum of the two reduction waves of dissolved oxygen. Polarogram *c* depicts the behaviour of the solution of polarogram *b* to which an amount of cobalt(II) corresponding to 0·05 g/l was added. Cobalt(II) obviates the inhibition effect of sodium hydroxide medium on the oxygen–sulphite reaction,

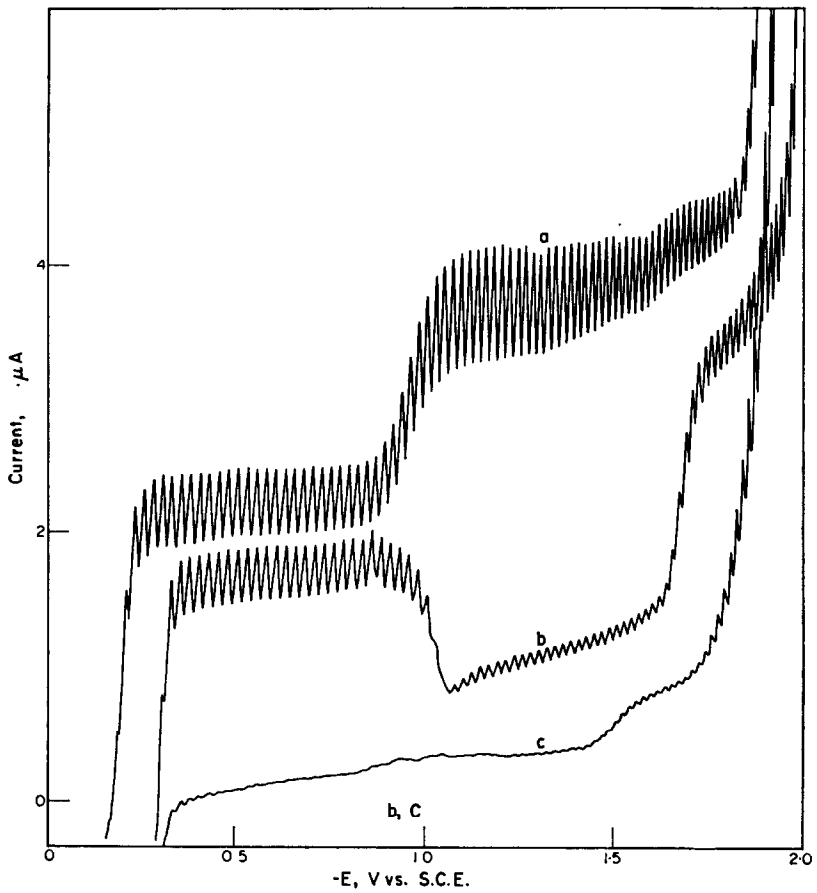

FIG. 1.—Polarograms of 1*F* NaOH and 0·005% gelatin supporting electrolyte, containing: (a) no addition; (b) 25 g/l Na_2SO_3; (c) 25 g/l Na_2SO_3 and 0·05 g/l Co(II).

irrespective of the tendency of cobalt to precipitate in this medium. Other alkali hydroxides, such as lithium or potassium hydroxides, display essentially the same behaviour as sodium hydroxide.

Some common solvents, such as ethanol and methyl cellosolve, inhibit the oxygen–sulphite reaction to some extent. Figure 2 depicts the behaviour of 1*F* potassium chloride in 30% v/v ethanol. The total diffusion current of both oxygen reduction waves displays an increase of 50% over that in polarogram *a* in Fig. 1. This is a reflection of increased oxygen solubility in aqueous ethanol medium and also of the increase of the rate of diffusion due to the low viscosity of potassium chloride in

aqueous ethanol, as compared to aqueous sodium hydroxide solution. When the solution also contained 25 g of sodium sulphite per l., substantial but incomplete de-oxygenation occurred (polarogram *b*). Further de-oxygenation was observed in polarogram *c* upon addition of 0·05 g of cobalt(II) per l., and bubbling nitrogen into the solution did not alter the shape of polarogram *c*. The appearance of a reduction

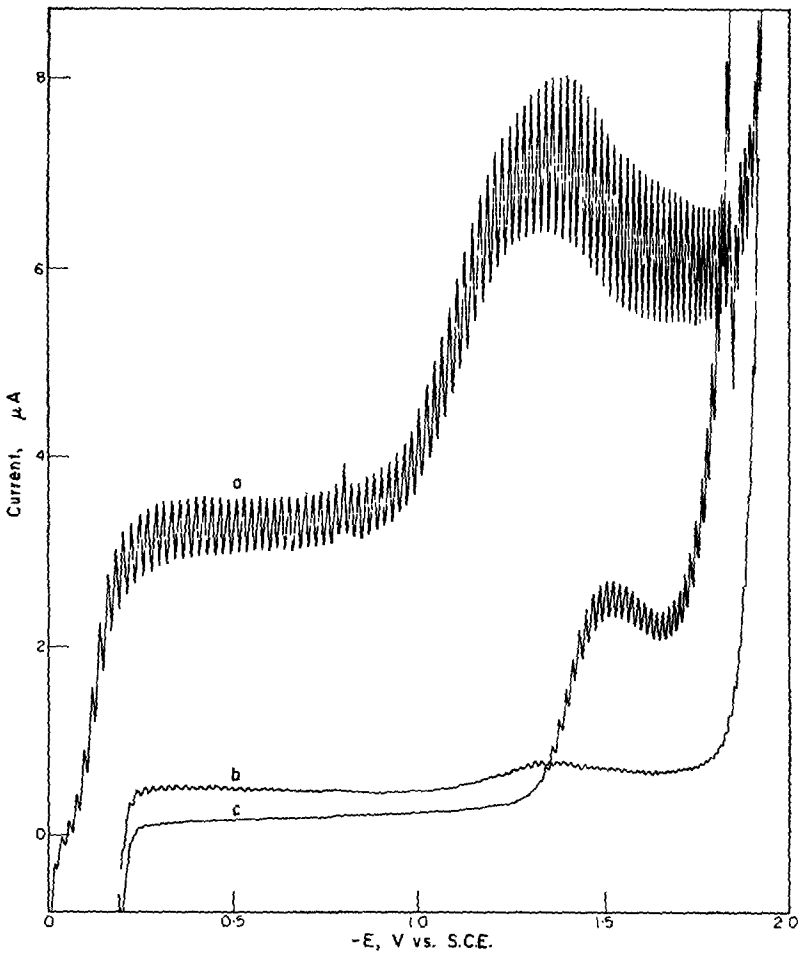

FIG. 2.—Polarograms of 1*F* KCl in 30% v/v ethanol–water supporting electrolyte, containing: (a) no addition; (b) 25 g/l Na_2SO_3; (c) 25 g/l Na_2SO_3 and 0·05 g/l Co(II).

wave at −1·4 V *vs.* S.C.E. was due to the reduction of cobalt(II). No inhibition of the oxygen–sulphite reaction was observed when 1*F* potassium chloride in aqueous solution or in 30% v/v acetone was employed.

The inhibition effect of EDTA is exhibited in Fig. 3. Polarogram *a*, obtained in 1*F* ammonia–ammonium chloride supporting electrolyte containing 0·01*F* EDTA, displays two oxygen reduction waves. Polarogram *b* was obtained after the inclusion of 25 g of sodium sulphite per l. Partial de-oxygenation of the solution occurred, but the distinct difference in magnitude of current of the two reduction waves demands

further elucidation. The oxidation of inhibitors in the presence of sodium sulphite has been reported in the literature,[8,12] and may lead to the formation of free hydrogen peroxide, thus increasing the second reduction wave of oxygen. A less probable explanation could be the formation of a reducible product of the inhibitor contributing to the second wave alone. When 0·05 g of cobalt(II) per l. was also included, complete de-oxygenation resulted (polarogram *c*).

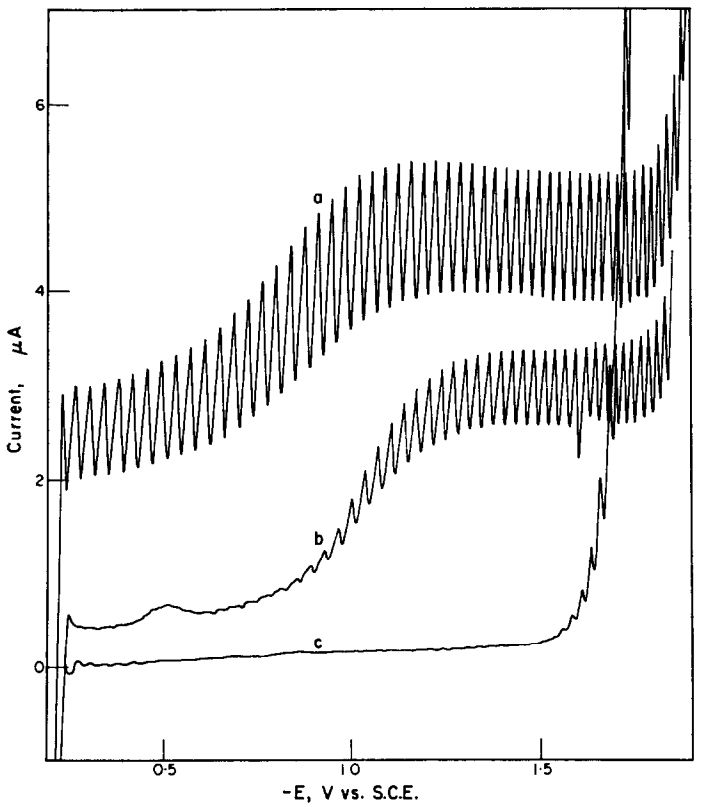

FIG. 3.—Polarograms of 1*F* NH_4OH, 1*F* NH_4Cl and 0·01*F* EDTA supporting electrolyte, containing: (a) no addition; (b) 25 g/l Na_2SO_3; (c) 25 g/l Na_2SO_3 and 0·05 g/l Co(II).

The addition of TEA to potassium chloride, or ammonia–ammonium chloride supporting electrolytes, strongly inhibits the oxygen–sulphite reaction (Fig. 4). Polarogram *a* was obtained with a solution consisting of 1*F* potassium chloride, 0·1*F* TEA and 25 g of sodium sulphite per l., whereon only partial de-oxygenation resulted. Complete de-oxygenation was obtained by the addition of 0·052 g of manganese(II) per l. to the solution (polarogram *c*). In the absence of sodium sulphite, manganese(II) (0·052 g/l.) eliminated only part of the dissolved oxygen present (polarogram *b*). The magnitude of the first reduction wave is higher than the second, since the product of oxidation of manganese(II), presumably manganese(IV), is reducible at positive potentials, contributing to the first oxygen wave. This is easily verified by de-oxygenation of the solution, by bubbling nitrogen through it, whereon

a single and smaller wave is obtained at the beginning of the polarogram. In the presence of sodium sulphite, however, no oxidation product of manganese(II) was observed in polarogram *c*.

It is to be noted that the addition of cobalt(II) or manganese(II) causes early depolarization of the dropping mercury electrode, possibly decreasing the hydrogen over-voltage, whereas the addition of sodium sulphite or EDTA causes anodic depolarization of mercury at a more negative potential (see corresponding polarograms

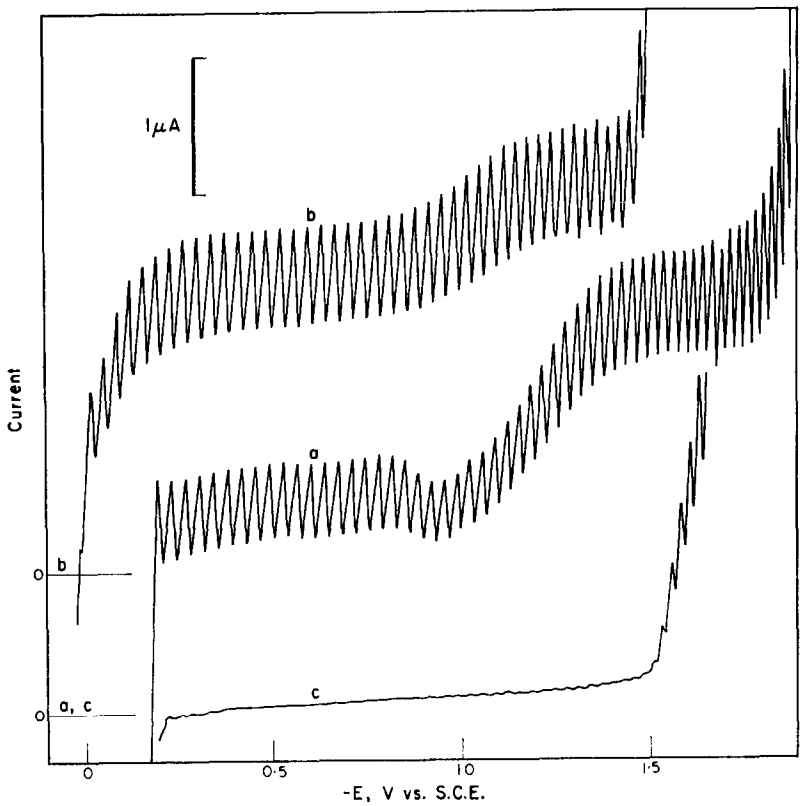

FIG. 4.—Polarogram of 1*F* KCl and 0·1*F* TEA supporting electrolyte, containing: (a) 25 g/l Na_2SO_3; (b) 0·052 g/l Mn(II); (c) 25 g/l Na_2SO_3 and 0·052 g/l Mn(II).

in all Figs.). In both cases, the useful range of potential span available for polarographic determination of active constituents is more limited. Even so, sodium sulphite can be utilized for de-oxygenation of the neutral and alkaline supporting electrolytes described when a large number of active constituents are determinable.

The polarograms, depicted in the presence of inhibitors and catalysts in this investigation, are time dependent. However, chronoamperometric study with the dropping mercury electrode at constant potential[7] makes it possible to follow the rate of disappearance of dissolved oxygen under various conditions. It can be shown that the rate of removal of oxygen increases with the increase in concentration of sodium sulphite and/or catalyst, and decreases with the increase in concentration of inhibitors.

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Zusammenfassung—Die Sauerstoff-Reduktionswellen werden zur Bestimmung des Inhibitionseffektes verwendet, den einige bei der Polarographie häufig zugesetzte Reagentien auf die Reaktion von gelöstem Sauerstoff mit Natriumsulfit in neutralen und alkalischen Trägerelektrolyten ausüben. Alkalimetallhydroxide, EDTA, TEA, Äthanol und Methylcellosolve hemmten die Reaktion in verschiedenem Ausmaß. In dieser Arbeit schien es, als könnten einige Metallionen wie Kobalt(II) und Mangan(II) die Sauerstoff-Sulfit-Reaktion katalysieren, was die Anwendbarkeit von Natriumsulfit zur Entfernung von Sauerstoff aus inhibitorhaltigen neutralen und alkalischen Trägerelektrolyten erweitern würde.

Résumé—On utilise les vagues de réduction de l'oxygène pour déterminer l'effet d'inhibition de quelques réactifs, communément ajoutés lors du travail polarographique, sur la réaction de l'oxygène dissous avec le sulfite de sodium dans des électrolytes-supports neutres et alcalins. Les hydroxydes de métaux alcalins, l'EDTA, la TEA, l'éthanol et le méthylcellosolve inhibent la réaction à des degrés divers. Dans ce travail, il est apparu que quelques ions métalliques, comme le cobalt (II) et le manganèse (II) peuvent catalyser la réaction oxygène-sulfite, permettant une application plus large du sulfite de sodium pour la désoxygénation d'électrolytes-supports neutres et alcalins contenant des inhibiteurs.

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DETERMINATIONS OF TRACES OF CALCIUM IN PHOSPHORIC ACID AND ITS SALTS BY ATOMIC-ABSORPTION SPECTROMETRY

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Summary—A method for the determination of traces of calcium by atomic-absorption spectrometry after extraction into an organic solvent, has been investigated for the determination of traces of calcium in phosphoric acid and its salts. Calcium is extracted as the hydroxyquinolate complex, the extract is introduced into the flame, and the calcium atomic-absorption is measured. The effects of pH, concentration of reagent, and diverse ions on the calcium extraction were investigated.

ATOMIC-ABSORPTION spectrometry has been applied to the determination of calcium in various kinds of sample. However, difficulty may be encountered in the determination of traces of calcium in phosphoric acid and its salts because of the effect of phosphate on the calcium absorption. For this kind of sample, it was considered preferable to combine the techniques of solvent extraction and atomic absorption, as had been done previously for magnesium[1], and this paper describes the results.

EXPERIMENTAL

Apparatus

A Hitachi photoelectric spectrophotometer EPU-2A was used with the atomic-absorption attachment RA-1. An air–acetylene flame was used with a 9-cm fishtail burner. Hitachi and Westinghouse hollow cathode lamps were used as light sources. The operating parameters were:

Air pressure	1·5 kg/cm²
Acetylene pressure	0·04 kg/cm²
Wavelength	4227 Å
Slit-width	0·03 mm
Lamp current	40 mA (Hitachi), 10 mA (Westinghouse).

Reagents

Calcium solution. Dissolve 0·250 g of calcium carbonate in a minimum excess of hydrochloric acid, and dilute to 100 ml with water.

8-*Hydroxyquinoline solution.* Dissolve 5 g of 8-hydroxyquinoline in 100 ml of ethanol.

Sodium tartrate solution, 10% w/v.

Saturated sodium chloride solution.

Buffer solution. Mix 1*M* potassium chloride solution and 1*M* sodium hydroxide solution to give a buffer of pH 13.

Reagents were of analytical grade unless otherwise stated.

Procedure

To 9·80 g of phosphoric acid in a polyethylene beaker, add 1 ml of 6*M* hydrochloric acid and 20 ml of sodium tartrate solution. Neutralize the solution by slowly adding 6*M* sodium hydroxide and dilute to 100 ml with water in a standard flask. Place 10 ml of this sample solution in a 50-ml separatory funnel, and add 10 ml of sodium chloride solution. Mix well, and then add 2 ml of butyl cellosolve, 3 ml of 8-hydroxyquinoline solution, and 5 ml of buffer solution. Adjust the volume to 40 ml, add exactly 5 ml of 3-methyl-1-butanol and shake vigorously for 1 min. Drain off and discard the aqueous phase. Spray the organic phase into the flame and measure the calcium absorption.

For phosphate samples, dissolve a suitable weight (3 g for diammonium hydrogen phosphate and 8·9 g for sodium pyrophosphate) in 2 ml of 1*M* hydrochloric acid and 20 ml of sodium tartrate solution, and dilute to 100 ml with water. Place 10 ml of the sample solution in a separatory funnel and proceed as above. If the pH of the solution is lower than 13, adjust it with sodium hydroxide before extraction.

Prepare a calibration curve by taking appropriate volumes of standard calcium solution in 50-ml separatory funnels, adding 10 ml of sodium chloride solution and 2 ml of sodium tartrate solution to each, mix, and apply the procedure.

RESULTS AND DISCUSSION

Atomic-absorption of calcium

The air–fuel ratio had a significant effect on the calcium absorption. The air pressure was set at a constant value (1·5 kg/cm^2), and the acetylene pressure was varied. The results are shown in Fig. 1. Although the acetylene pressure which gives maximum

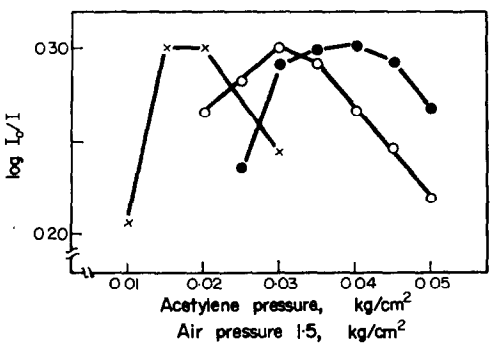

FIG. 1.—Effect of acetylene pressure on calcium absorption
Beam height above burner top: ×—2·0 mm; ○—3·0 mm; ●—4·5 mm.

absorption depends on the beam height above the burner-top, the maximum absorption was constant irrespective of the beam height.

Extraction of calcium

Extraction of calcium hydroxyquinolate has been used for spectrophotometric determinations,[2–4] and we investigated the use of various solvents such as 3-methyl-1-butanol, 4-methyl-2-pentanone, butyl acetate, 1-butanol and chloroform. Of all the solvents tested 3-methyl-1-butanol was found to be best for extraction because it gave a higher sensitivity of measurement. The extraction efficiency was estimated by extracting with successive 5-ml portions of 3-methyl-1-butanol. It was found that 89% of the calcium was extracted in a single pass, over the range of calcium concentration studied. In the present work, a single extraction was used because it was highly reproducible. Shaking vigorously for longer than a minute did not improve the extraction. Although calcium hydroxyquinolate could be extracted into 3-methyl-1-butanol, the addition of butyl cellosolve resulted in better extraction and repeatability for increasing amounts of calcium. Some workers[2,4] have successfully extracted calcium hydroxyquinolate complex with chloroform by using butyl cellosolve as a supplementary solvent. However, chloroform gives an unstable flame and noxious gases during the combustion. Solvents other than esters, ketones and alcohols were not suitable for atomic-absorption measurements because of incomplete combustion and self-absorption of radiation.

The extraction of calcium hydroxyquinolate was examined over a pH range of 10·0–13·6. The degree of extraction was constant when the pH was greater than 12·5. The effect of reagent concentration on the degree of extraction was also investigated. The degree of extraction was constant if more than 100 mg of 8-hydroxyquinoline were added.

Sodium chloride was useful for salting-out and preventing emulsification, the minimum necessary for reproducible results being 5 ml of saturated sodium chloride solution in 40 ml of aqueous phase. Tartrate, which served to prevent the formation of calcium phosphate at higher pH, had no effect on the extraction of calcium when present in concentrations of 0·01–0·05*M*.

The calibration curves are almost linear and were corrected for a very small blank value which we attributed to absorption caused by 8-hydroxyquinoline.

Various metals form hydroxyquinolate complexes at pH 13, some of which are extractable into 3-methyl-1-butanol. To ascertain the influence of diverse ions on extraction and on the calcium atomic-absorption in the flame, calcium was extracted with 8-hydroxyquinoline from solutions containing diverse ions; Al (489 μg), Ba (1063 μg), Cr (456 μg), Cu (532 μg), Fe (989 μg), Mg (1004 μg), Mn (511 μg), Mo (320 μg), Ni (964 μg), Pb (801 μg), Si (1554 μg), Sn (654 μg), Sr (1440 μg), Ti (497 μg), W (1000 μg) and Zn (1266 μg) did not interfere in the determination of 40 μg of calcium. Aluminium and titanium depressed the calcium absorption when an aqueous solution was sprayed into the flame, but no interference was observed in the present method, even though both metals were extracted into the organic phase as hydroxyquinolates. It may be considered that 8-hydroxyquinoline in the extracts counteracts the depressive effect of aluminium and titanium on the calcium absorption. Larger amount of these metals did cause depression of the calcium absorption. Large amounts of chromium and molybdenum also affected the calcium absorption, but this effect could be controlled by changing the air–fuel ratio, a fuel-rich flame being recommended. The copper complex remained in the aqueous phase as a precipitate and did not dissolve in 3-methyl-1-butanol, but resulted in a lower result for the calcium. A complexing agent such as cyanide was necessary to keep copper in solution. Traces of calcium could be extracted from solutions containing large amounts of phosphate (100 mg of P) without loss.

Attempts to use 8-hydroxyquinaldine as complexing agent were unsuccessful. The atomic-absorption of the calcium in the flame was very low, and it was concluded that the calcium was very incompletely extracted into the solvents tried (3-methyl-1-butanol, 4-methyl-2-pentanone, butyl acetate, amyl acetate and 1-butanol).

Determination of traces of calcium in phosphoric acid and its salts

Table I shows the results for some samples of phosphoric acid and phosphates. One sample was analysed five times to evaluate the reproducibility of the method. The mean value was found to be 13·5 ppm and the coefficient of variation was 3·7%. Recovery of added calcium was excellent. Earlier workers[5,6] have described the determination of calcium in phosphoric acid, but the present method appeared to be very convenient for traces of calcium in phosphoric acid and its salts.

Application of the method to polypropylene polymers

Polypropylene polymers contain titanium, aluminium and phosphorus together with calcium derived from additives or the polymerization catalyst. The present

TABLE I.—DETERMINATION OF TRACES OF CALCIUM IN PHOSPHORIC ACID AND ITS SALTS

Sample	Calcium, *ppm*	
	Added	Found
Phosphoric acid A	—	13·2, 13·3
	20·0	32·9
Phosphoric acid B	—	1·6, 1·6
	20·0	21·5
Diammonium hydrogen phosphate	—	15·4, 15·4
	133·5	149
Sodium pyrophosphate	—	3·2, 3·2
	22·4	25·6

extraction method was applied to the determination of calcium in such samples. For estimation 1 g of sample was ashed in a platinum crucible with 0·3 g of sodium carbonate. After addition of 6M hydrochloric acid to acidify the residue, the contents of the crucible were heated with 20 ml of sodium tartrate solution to give a clear solution which was then diluted to 100 ml, and 10 ml of this solution were used for analysis.

TABLE II.—DETERMINATION OF CALCIUM IN POLYPROPYLENE POLYMERS

Polypropylene	Calcium, *ppm*	
	Added	Found
A	—	45, 45
	100·0	146
B	—	120, 120
	200·0	324
C	—	267, 267
	200·0	460

The results obtained for some polymers are shown in Table II. Calcium in polymers can be determined only with difficulty by the usual method because of the low content of calcium and the presence of titanium, aluminium and phosphorus. The present method is convenient for measuring the calcium.

Résumé—On a étudié une méthode de dosage de traces de calcium par spectrométrie d'absorption atomique après extraction en solvant organique pour doser des traces de calcium dans l'acide phosphorique et ses sels. On extrait le calcium à l'état de complexe hydroxyquinoléinique, introduit l'extrait dans la flamme et mesure l'absorption atomique du calcium. On a étudié les influences du pH, de la concentration du réactif et de divers ions sur l'extraction du calcium.

Zusammenfassung—Ein Verfahren zur Bestimmung von Calciumspuren durch Atomabsorptionsspektrometrie nach Extraktion in ein organisches Lösungsmittel wurde zur Bestimmung von Calciumspuren in Phosphorsäure und ihren Salzen geprüft. Calcium wird als Hydroxychinolatkomplex extrahiert, der Extrakt in die Flamme gebracht und die Atomabsorption von Calcium gemessen. Der Einfluß von pH, Reagenskonzentration und verschiedenen Ionen auf die Extraktion von Calcium wurden untersucht.

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HOMOGENEOUS NUCLEATION OF MAGNESIUM HYDROXIDE†

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Summary—The rate of homogeneous nucleation of magnesium hydroxide has been determined as a function of solution concentration, using a quasi-homogeneous precipitation technique and electronic particle counting. The nucleation rate becomes measurable at supersaturations of about 4, and is dependent on the 33rd power of the product $a_{Mg}a_{OH}^2$. The experimental results are consistent with nucleation theory. The nucleus–solution interfacial energy is calculated to be 115 erg/cm^2.

THE rate of homogeneous nucleation of magnesium hydroxide precipitating from solution may be written[1]

$$dN/dt = k(IP)^n$$

where N = number of nuclei formed, t = time, (IP) = ion product = $a_{Mg}a_{OH}^2$, and n = number of $Mg(OH)_2$ units in the nucleus. Determination of the rate of nucleation as a function of the ion product thus provides a conceptually simple means for determining the size of the precipitation nucleus. Because nucleation is a very high order rate process, this approach is useful only if the ion product can be varied within quite narrow limits. The approach has been successfully applied to a study of strontium sulphate nucleation,[1] the results of which gave strong support to current nucleation theory, as developed by Nielsen.[2] The approach and techniques of the strontium sulphate study have been modified and applied to the magnesium hydroxide system, a system of some commercial importance because of the occurrence of this material in scale deposits.

EXPERIMENTAL

Magnesium ion and hydroxide ion were generated simultaneously, in stoichiometric amounts, by electrolysis of a 0·10*M* solution of sodium nitrate with a magnesium anode and a platinum cathode. The electrolysis current was 1 mA and the solution volume was about 200 ml, so the concentration of magnesium hydroxide was increasing at the rate of $2{\cdot}6 \times 10^{-8}$ mole l^{-1} sec^{-1}. The electrolysis cell was a jacketed beaker thermostatically kept at 25·0°.

Precautions were taken to keep carbon dioxide out of the system, and to remove most (if not all) of the foreign particles from the solution. The latter was accomplished by continuously pumping the solution from the cell through a fibreglass filter mat and back into the cell. After a few hours of filtration the number of foreign particles dropped to a few thousand per cm^3, as determined with the Coulter particle counter, the filtering system was closed off from the cell, and electrolysis was begun.

The solution concentration was monitored by pH measurement. A Sargent glass–calomel combination electrode was placed in the solution as far as possible from the electrolysis electrodes, and was also surrounded by a grounded platinum screen. With these precautions the electrolysis current did not affect the pH reading. The pH was recorded with scale expansion of such sensitivity that pH changes of 0·001 pH could be measured.

At intervals during the electrolysis a 3-ml portion was removed, and the number of particles present in it was counted, using a Coulter electronic particle counter with a 30-μ orifice.

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RESULTS AND DISCUSSION

The pH measurements indicated that the precipitation of magnesium hydroxide in these experiments followed the typical pattern for precipitations from homogeneous solution[3,4]—an increase in concentration to beyond the saturation concentration, and then a decrease as nucleation began to occur at a rate sufficient to cause rapid precipitation. The maximum pH obtained was 11·186 and represents the pH at which the rate of removal of magnesium hydroxide by crystal growth was equal to the rate of electrolytic generation of magnesium hydroxide.

Each experiment yielded two plots, one of pH as a function of time and one of number of particles as a function of time. The maximum rate of formation of particles occurs at the maximum pH, but because of the nature of the counting instrument, particles are not detected until some time after they are formed, and so the maximum in the rate of production of particles does not appear to the detector until well after the pH has reached its maximum value. Nuclei are only a few Å in diameter, but particles cannot be counted until they are a few hundred mμ in diameter, and so the number–time plot will lag behind the pH–time plot by the amount of time necessary for the nuclei to grow to detectable size. In the present experiments the apparent maximum rate of production of particles was observed by the detector about 30 min after the solution had reached its maximum pH. The number–time curves were then reconciled with the pH–time curves by shifting the time axes so that the maximum rate of production of particles occurred at the maximum pH. This assumes that the rate of production of particles is the same as the rate of nucleation, or that each nucleus, whenever it was formed, requires the same amount of time to grow to observable size, regardless of the solution concentration. This assumption is clearly wrong, because the nuclei formed earlier grow in a more concentrated solution than those formed later, and so will reach observable size more quickly. However, the pH change during the period under consideration is only about 0·06 and this small change in the hydroxyl ion concentration, coupled with the fact that crystal growth is a much lower order rate process than nucleation, makes the uncertainty from this approximation rather small.

Figure 1 shows the results of a typical experiment; the time axis of the number–time plot has been shifted as described above. Nucleation occurred at conveniently measurable rates only at pH values above 11·170. The ion product, $a_{M_g}a_{OH}^2$ was calculated from the pH, the sequence of calculations being as follows: (1) the activity of the hydroxyl ion, a_{OH}, was calculated from the pH, (2) the ratio a_{M_gOH}/a_{M_g} was calculated from a_{OH}, using 4×10^2 as the formation constant for the complex MgOH,[5] (3) the ratio [MgOH]/[Mg] was calculated from a_{M_gOH}/a_{M_g}, using 0·80 and 0·45 as estimates of the activity coefficients of MgOH and Mg, respectively, (4) [OH] was calculated from a_{OH}, using 0·76 as the activity coefficient for OH, (5) [Mg] was calculated from [OH] and [MgOH]/Mg], by means of the equation

$$2([Mg] + [MgOH]) = [OH] + [MgOH],$$

which results from the generation of Mg and OH in equivalent amounts, (6) a_{M_g} was calculated from [Mg], (7) (*IP*), the ion product was calculated as $a_{M_g}a_{OH}^2$. The results of four experiments are presented in Fig. 2, a plot of log dN/dt against log (*IP*). Values of (*IP*) were calculated as indicated above, and dN/dt values were obtained by taking the slopes of the number–time plots at various pH values. The

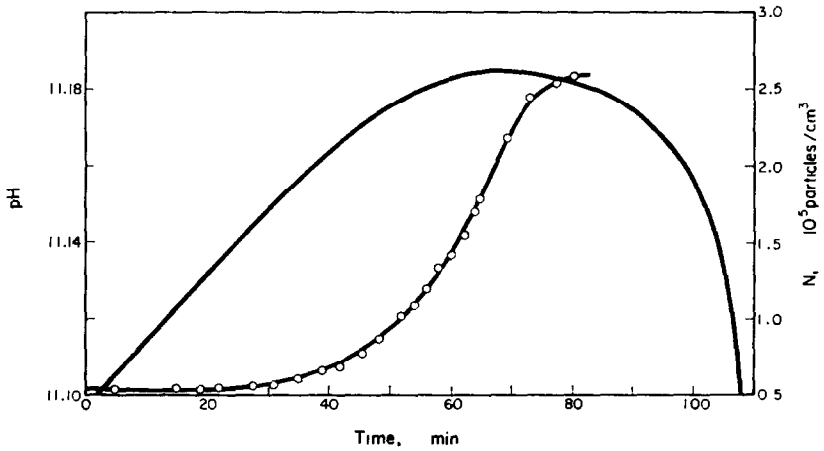

FIG. 1.—Variation with time, of pH [upper curve] and of number of particles, during an experiment.

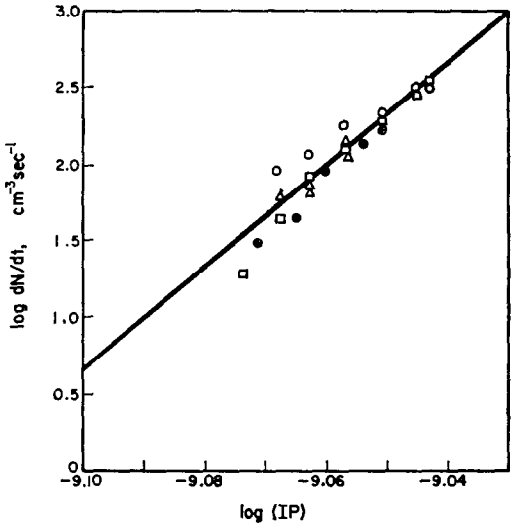

FIG. 2.—Dependence of rate of nucleation [particles/cm^{3}sec] on solution concentration expressed as $(IP)[a_{Mg}a_{OH}{}^2]$.

least-squares slope for the points of Fig. 2 is 33 $\pm$ 4 (90% confidence limits) and so the best value for the number of $Mg(OH)_2$ units in the nucleus is 33.

To confirm that the process observed was homogeneous nucleation, a comparison between experiment and theory was made. From Fig. 2, $\log dN/dt = 2{\cdot}98$ at $\log(IP) = -9{\cdot}030$. The theoretical expression for the rate of homogeneous nucleation may be expressed as:[2]

$$dN/dt = (D/d^2 v_0)(2\phi/3\pi kTn^*)^{1/2} \exp(-\Delta G^*/kT),$$

where dN/dt = rate of nucleation = 10^8 ml^{-1} sec^{-1}

D = diffusion coefficient of $Mg(OH)_2 = 2 \times 10^{-5}$ (estimated from values for $Ca(OH)_2$ and $Ba(OH)_2$]

d = mean diameter of one Mg and two OH ions = 5×10^{-8} cm (estimated from Debye-Hückel hydrated ion diameters)

v_0 = molecular volume of solvent = 3×10^{-23} cm^3

$\phi = kT \ln S = kT \ln [(IP)/K_{sp}]^{1/3}$; $\log K_{sp} = -10{\cdot}90^5$ and $\log (IP) = -9{\cdot}030$, so $\phi = 1{\cdot}43\ kT$

n^* = number of ions in the nucleus = 3×33

ΔG^* = free energy of nucleation.

This kinetic method yields $\Delta G^* = 64{\cdot}6\ kT$. A thermodynamic value for ΔG^* may be calculated from Gibb's equation

$$\Delta G^* = \phi n^*/2 = 70{\cdot}7\ kT$$

The thermodynamic and kinetic values for ΔG^* differ by less than 10%, an agreement which is satisfactory but not overwhelming. Exact agreement between the two values would be obtained for a nucleus of 30 $Mg(OH)_2$ units, well within the experimental error of the 33 found in this study.

ΔG^* may also be related to the nucleus–solution interfacial tension through the equation[2]

$$\Delta G^* = \phi n + \sigma A,$$

where σ = interfacial tension, and A = surface area of the nucleus.

The volume of 33 $Mg(OH)_2$ units in the crystal is $1{\cdot}3 \times 10^{-21}$ cm^3; this volume could be occupied by a sphere with $A = 6 \times 10^{-14}$ cm^2, a cube with $A = 7{\cdot}2 \times 10^{-14}$ cm^2, or a rectangular parallelepiped with edge lengths proportional to unit cell dimensions, with $A = 7{\cdot}7\ 10^{-14}$ cm^2. Assuming, with no experimental basis, that the parallelepiped is correct, σ is calculated to be 115 erg/cm^2.

In 1942, Gjaldback[6] determined the K_{sp} of $Mg(OH)_2$, using a precipitation method. He reported an "active" phase of $Mg(OH)_2$ with $\log K_{sp} = -9{\cdot}2$. The present study indicates that a concentration corresponding to this K_{sp} is required to initiate homogeneous nucleation, and it may therefore be concluded that the "active" phase is the $Mg(OH)_2$ homogeneous nucleus.

Zusammenfassung—Die Geschwindigkeit der homogenen Keimbildung von Magnesiumhydroxid wurde in Abhängigkeit von der Lösungskonzentration mit Hilfe eines quasihomogenen Fällungsverfahrens und elektronischer Teilchenzählung bestimmt. Die Keimbildungsgeschwindigkeit wird bei Übersättigungen von etwa 4 meßbar und hängt von der 33. Potenz des Produkts $a_{Mg}a_{OH}{}^2$ ab. Die experimentellen Ergebnisse sind in Einklang mit der Keimbildungstheorie. Die Grenzflächenenergie Keim-Lösung wird zu 115 erg/cm^2 berechnet.

Résumé—On a déterminé la vitesse d'amorçage homogène de l'hydroxyde de magnésium en fonction de la concentration de la solution, en utilisant une technique de précipitation quasi homogène et un comptage de particule électronique. La vitesse d'amorçage devient mesurable à des sursaturations d'environ 4, et dépend de la 33^e puissance du produit $a_{Mg}a_{OH}{}^2$. Les résultats expérimentaux sont conformes à la théorie de l'amorçage. On a calculé que l'énergie interfaciale amorce-solution est de 115 erg/cm^2.

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SPECTROPHOTOMETRIC DETERMINATION OF NITRATE WITH *p*-DIAMINODIPHENYLSULPHONE AND DIPHENYLAMINE–*p*-DIAMINODIPHENYLSULPHONE

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Summary—*p*-Diaminodiphenylsulphone is used in a new spectrophotometric method for the determination of nitrate. Factors affecting the colour development are given. The useful range for a 1-cm cell is 30–300 mg/l. In this range the coloured solutions are stable and obey Beer's law. The method is rapid and precise and is applicable to routine analysis of samples containing macro amounts of nitrates. For determination of micro amounts of nitrate the reagent is modified by addition of diphenylamine. The limit of determination is then 0·25 mg/l at 15°. This method can be considered specific for nitrate and is applicable in the presence of nitrite.

ALTHOUGH many methods for nitrate determination are known and used,[1–6] most of them are either subject to numerous interferences or are difficult to use. There is a need for a new method which is accurate and rapid.

EXPERIMENTAL

Reagents

p-*Diaminodiphenylsulphone solution.* Dissolve 2 g of pure 4,4′-diaminodiphenylsulphone(DDS) in 1000 ml of reagent-grade concentrated sulphuric acid. The reagent is colourless and stable for several months.

Standard nitrate stock solution (1000 *ppm* NO_3^-). Dissolve in water 1·630 g of dried potassium nitrate (reagent-grade) and dilute to 1000 ml. Prepare working standard nitrate solutions by suitably diluting the stock standard solution.

Procedure

By pipette transfer to a test-tube 1 ml of halide-free sample solution, containing 30–300 ppm of nitrate, and add dropwise with continuous stirring 4 ml of DDS reagent and continue stirring for several seconds to ensure intimate mixing. Put the tube in a water-bath, heat to boiling, and let stand for 2 min. Cool the tube to room temperature, dilute the solution accurately to 25 ml, mix, and read the absorbance at 410 mμ in a 1-cm cell. As a blank use either 4 ml of reagent diluted to 25 ml or approximately 3*M* sulphuric acid. Determine the nitrate content of the sample from a calibration curve covering the range 30–300 μg of nitrate per ml of sample. Beer's law is obeyed over this range, and the colour is stable. The molar absorptivity is 2400.

The absorption spectrum is shown in Fig. 1.

RESULTS AND DISCUSSION

When DDS reagent is added to nitrate 3,3′-dinitro-4,4′-diaminodiphenylsulphone is formed; this is a yellow dye, stable in acid. The procedure is simple and accurate. It is not necessary to dry the samples or to add a base for the colour development. The interference of halides must be removed by adding solid silver sulphate and then filtering. Table I shows the average, range and maximal deviation for a series of five consecutive nitrate determinations, for each concentration shown.

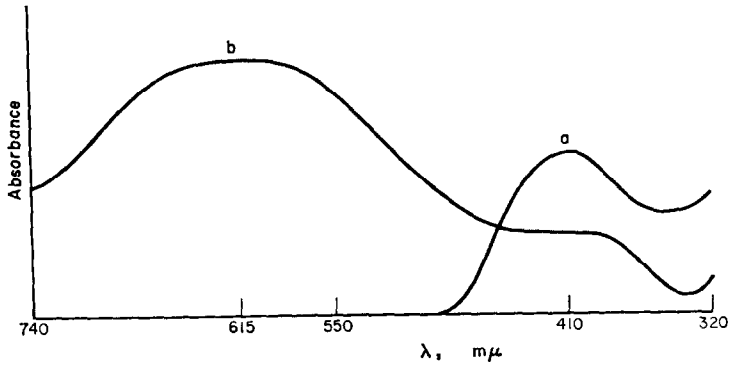


FIG. 1.—Absorption spectra of the reaction products.
a—*p*-diaminodiphenylsulphone reagent; *b*—diphenylamine–*p*-diaminodiphenylsulphone reagent.

TABLE I

Nitrate taken, *ppm*	Nitrate found, *ppm*					Average, *ppm*	Max. deviation, *ppm*
30	30	29	28	32	29	30	2
60	61	58	59	60	61	60	2
100	99	102	99	100	101	100	2
200	200	202	199	201	200	200	2
300	299	297	296	298	298	298	4

Effect of time and temperature

The reagent was added dropwise from a burette to 1 ml of 100 ppm nitrate solution with continuous stirring to avoid local over-heating. The temperature of the mixture rose to 60–70° and some colour developed.

When the solutions were allowed to stand at room temperature for 15, 30, 60 and 120 min and were then diluted and measured, the results in Table II were obtained.

TABLE II

Time, *min*	Absorbance	Colour development, %
15	0·235	76
30	0·290	94
60	0·310	100
120	0·310	100

When the solutions were placed in a cold water-bath, heated to boiling, cooled, diluted and measured, the results shown in Table III were obtained.

TABLE III

Time from start of boiling, *min*	Absorbance	Colour development, %
0	0·300	96
2	0·310	100
5	0·310	100
10	0·310	100

If the test-tubes were cooled in tap water while the reagent was added, no colour development had occurred at the end of mixing but after heating *etc.* the same colour intensity was obtained as before.

Interferences

Table IV shows the effect of other species. The nitrate concentration of the test solutions was 100 ppm after addition of the interfering substances.

Substances which cause a decrease in colour intensity are listed as negatively interfering, and those which cause an increase (mostly due to incompatibility with the concentrated sulphuric acid) are listed as positively interfering.

TABLE IV

Substance	Concentration, *ppm*	Effect
K^+, Na^+, NH_4^+	1000	none
Ca^{2+}, Mg^{2+}	500	none
Mn^{2+}, Zn^{2+}	100	none
Al^{3+}	500	none
Cr^{3+}	100	none
Co^{2+}	20	none
Fe^{3+}	20	none
Fe^{2+}	20	negative
Cu^{2+}	50	none
Hg^{2+}	500	none
Pb^{2+}	20	none
MoO_4^{2-}	20	none
CrO_4^{2-}	100	none
Ag^+	500	none
Cl^-, SCN^-	20	negative
Br^-, I^-	20	positive
Cl_2, Br_2	20	positive
BrO_3^-, IO_3^-	50	positive
PO_4^{3-},	500	none
BO_3^{3-}	100	none
SO_3^{2-}	500	none
$S_2O_3^{2-}$	500	none
$S_4O_6^{2-}$	500	none
NO_2^-	20	positive
Urea	50	none
Sulphamic acid	100	negative
Chloroform	large amounts	none
Aliphatic amines	large amounts	none
Aliphatic amino-acids	large amounts	none
Aliphatic amino-alcohols	large amounts	none
Pyridine	large amounts	none
Methanol, ethanol		negative
Propanol, butanol		negative
Ethyl acetate		negative

Halides are removed as the silver salts. Chlorine, bromine, bromate and iodate must be reduced with bisulphite and the reduction product removed with solid silver sulphate. Iron(II) is oxidized with ammonium persulphate. Nitrite is removed with a small excess of urea, but not with sulphamic acid, which itself interferes.

Conclusion

The low sensitivity of the method makes it possible to determine relatively large amounts of nitrate, with relatively few interferences. The existing volumetric and

gravimetric methods are subject to numerous interferences. The chief advantages of this method are its accuracy and rapidity. The whole determination takes less than half an hour even when halides *etc.* must be removed.

For microdeterminations the reagent must be modified by addition of diphenylamine, as described below.

DIPHENYLAMINE–*p*-DIAMINODIPHENYLSULPHONE METHOD

EXPERIMENTAL

Reagent

*Diphenylamine–*p*-diaminodiphenylsulphone solution.* Take 225 ml of water in a 1-l. beaker, add 50 mg of diphenylamine (reagent-grade) and 2 g of *p*-diaminodiphenylsulphone (pure), and mix well; add slowly, while continuously stirring, 600 ml of nitrate-free, colourless concentrated sulphuric acid. Allow to cool, add 100 ml of concentrated phosphoric acid (reagent-grade), transfer to a 1-l. volumetric flask, and make up to the mark with concentrated sulphuric acid. The solution is colourless and stable for several months.

Sodium chloride solution (approximately 20,000 ppm Cl^-). Dissolve 3·3 g of sodium chloride (reagent-grade) in 100 ml of water.

Procedure

By pipette transfer 1 ml of sample containing 0·25–2, 0·3–2·5 or 0·4–3 μg of nitrate ion (depending on the working temperature) and 0·5–5 mg of chloride ion into a 25-ml Erlenmeyer flask cooled in ice-water; add very slowly, by burette or pipette, 10 ml of reagent, while continuously stirring, and continue stirring for several seconds to ensure intimate mixing. Allow the flask to stand in ice-water during the reagent addition and for 30 min more, and afterwards keep it at room temperature or in a thermostat. Read the intensity of the blue colour at 600 mμ in a 1-cm cell. Use as blank a mixture of 1 ml of sodium chloride solution (containing 500–5000 ppm of chloride) and 10 ml of reagent.

Determine the nitrate content of the sample from a calibration curve when working at constant temperature (thermostat) or by comparison with a standard solution (preferably 1·5 ppm of nitrate) when working at room temperature.

Calibration curve

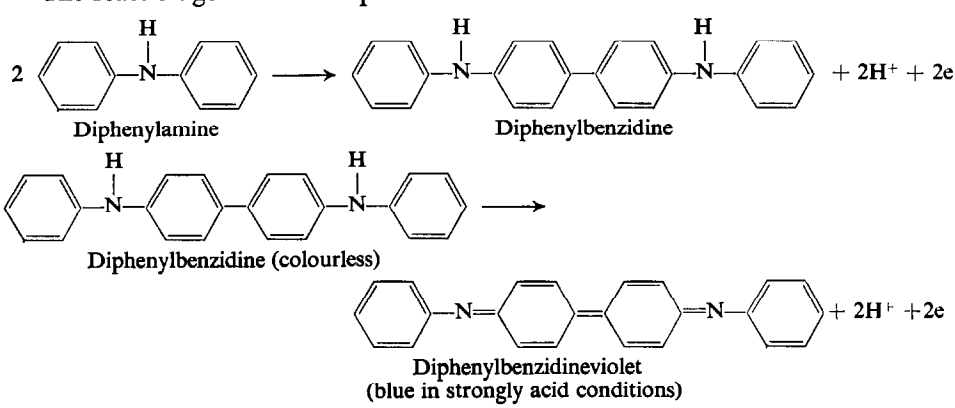
Standards are prepared covering the range 0·25–3 μg of nitrate per ml of solution by suitable double dilution of the 1000-ppm nitrate standard, and are treated as described above. Colour stability is obtained in 1½–2½ hr (depending on the temperature); the intensity of the colour remains constant for at least as long as the time of development and the system obeys Beer's law, over the ranges 0·25–1·7 ppm at 15°, 0·30–2·2 ppm at 20° and 0·40–2·7 ppm at 25–30°.

The molar absorptivity is 300×10^3 at 15° and 170×10^3 at 25–30°C. The absorption spectrum gives a plateau maximum from 590 to 615 mμ (Fig. 1).

RESULTS AND DISCUSSION

When the reagent is added to nitrate the oxidation product of the diphenylamine is developed and a blue coloration results.

The reaction goes in two steps:[7]



In the various methods in which diphenylamine is used for colorimetric estimation of the nitrate ion, it is nearly impossible to obtain stability in colour development. There is a rapid initial increase of intensity followed by a decrease and a colour change to (green absorption peak at 450 mμ). Beer's law is not followed. The *p*-diaminodiphenylsulphone in the mixed reagent stabilizes the colour for at least 1½–2½ hr and accurate readings can be taken, see Fig. 2.

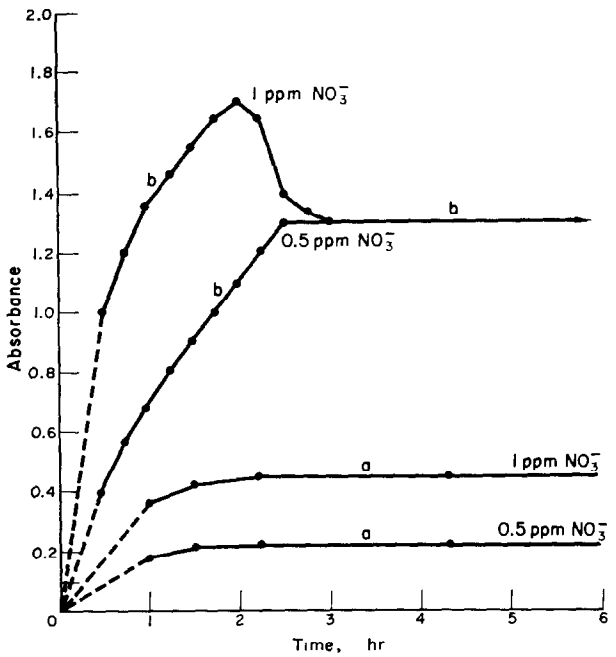


FIG. 2.—Stabilization of colour by use of mixed reagent.
a—Diphenylamine-*p*-diaminodiphenylsulphone reagent;
b—Diphenylamine reagent.

The dependence of the colour development on time, temperature, and the presence of chloride, is shown in Tables V and VI and Fig. 3.

TABLE V.—INFLUENCE OF CHLORIDE CONCENTRATION ON COLOUR DEVELOPMENT AT 15°C

$[Cl^-]$, *ppm*	Absorbance	Degree of colour development, %
0	0	0
20	0·28	62
100	0·42	93
200	0·43	95
500	0·45	100
1000	0·45	100
2000	0·45	100
5000	0·45	100
10000	0·45	89
20000	0·34	76
100000	0·27	60

TABLE VI.—INFLUENCE OF TIME AND TEMPERATURE

Temperature, °C	Nitrate taken, *ppm*	Nitrate found, *ppm*					Average, *ppm*	Range, *ppm*	Error, %
15	0·25	0·23	0·24	0·25	0·25	0·24	0·24	±0·02	−3·2
15	0·50	0·51	0·50	0·49	0·50	0·49	0·50	±0·01	—
15	1·00	1·00	1·02	1·00	0·98	1·00	1·00	±0·02	—
15	1·50	1·48	1·50	1·50	1·52	1·46	1·49	±0·04	−0·6
15	2·00	1·93	1·91	1·89	1·91	1·93	1·91	±0·11	−4·5*
20	0·30	0·30	0·29	0·28	0·31	0·29	0·29	±0·02	−2·0
20	1·50	1·49	0·50	0·51	0·51	0·50	1·50	±0·01	—
20	2·00	2·03	2·00	2·03	2·00	2·03	2·02	±0·03	+1·0
20	2·50	2·45	2·38	2·38	2·42	2·45	2·42	±0·12	−3·3*
30	0·40	0·39	0·41	0·40	0·38	0·40	0·40	±0·02	—
30	1·50	1·51	1·49	1·50	1·52	1·51	1·51	±0·02	+0·6
30	2·50	2·47	2·50	2·44	2·50	2·47	2·48	±0·06	−0·8
30	3·00	2·94	2·88	2·90	2·94	2·92	2·92	±0·12	−2·7*
40	0·40	0·39	0·42	0·38			0·40	±0·02	—
40	1·50	1·55	1·58	1·55			1·56	±0·08	+4·0
40	2·50	2·45	2·55	2·60			2·53	±0·10	+4·0
40	3·00	2·85	2·90	2·86			2·87	±0·13	−4·3*

* Deviation from Beer's law.

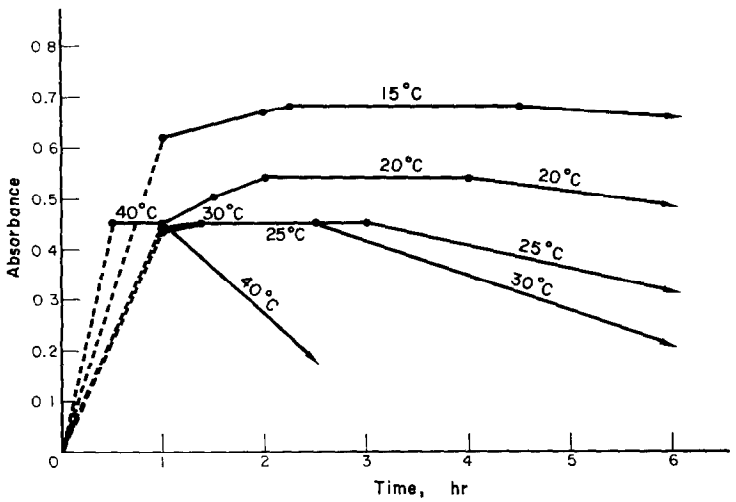


FIG. 3.—Influence of time and temperature on absorbance resulting from 1·5 ppm of nitrate.

Interferences

Only a few substances affect the colour development. If possible, coloured solutions should be decolorized and filtered; otherwise a mixture of 1 ml of sample and 10 ml of approximately 80% sulphuric acid is used as a comparison blank. Though diphenylamine is an intense and sensitive redox indicator, oxidizing agents have a relatively slight effect on the colour development with this reagent. Results obtained with various oxidants are shown in Table VII.

TABLE VII.—INFLUENCE OF OXIDANTS ON DETERMINATION OF 1 ppm OF NITRATE AT 15°C

Substances added, *ppm*		Nitrate found, *ppm*		
		A	B	C
	—	0·80	1·00	1·00
$Na_2S_2O_8$	20	0·80	1·00	1·00
$Na_2S_2O_8$	200	0·84	1·04	1·04
$(NH_4)_2S_2O_8$	20	0·82	1·02	1·02
$(NH_4)_2S_2O_8$	200	0·84	1·07	1·11
$(NH_4)_2S_2O_8$	1000	0·52	1·25	1·67
$Fe_2(SO_4)_3$	10	0·80	1·00	1·00
K_2CrO_4	1	0·80	1·00	1·00
K_2CrO_4	5	0·82	1·02	1·02
Cl_2	5	0·82	1·02	1·02
H_2O_2	10	1·28	1·73	1·73

Readings were taken after 1 hr (A), 2½ hr (B) and 3½ hr (C); the results are the averages of 3 determinations.

Though small amounts of strong oxidizing agents other than peroxides have little effect, for precise work it is best to remove them. This can be done by taking an aliquot (10–50 ml) of sample, acidifying it with dilute sulphuric acid, adding potassium iodide and starch solution and titrating with 0·05*N* sulphite until colourless; then to another aliquot of sample the same volume of sulphite solution is added and this solution is then used for the nitrate determination. A small excess (10–20 ppm) of sulphite does not interfere.

Any iron(III) present is also reduced to iron(II) and interferes by reducing nitrate in acid conditions. The iron(III) can be removed by ion-exchange or the iron(II) reoxidized with a small excess of sodium persulphate or potassium permanganate.

Permanganate can be used to destroy peroxides, the excess of it being removed with oxalate. Any nitrite present then interferes because of its oxidation to nitrate, and a correction must be applied for the amount of the nitrate found by a suitable nitrite determination. Nitrite ion generally interferes more or less in all colorimetric nitrate determination methods except this one, where it reacts quantitatively with the *p*-diaminodiphenylsulphone (diazotization).[8] Samples containing 0·1–1 ppm of nitrite remain colourless on reagent addition; samples containing 10 ppm give an initial violet colour which vanishes on further addition of reagent; a blue colour develops only if the sample also contains nitrate. The effect of nitrite is shown in Table VIII.

Most of the inorganic acids, and organic acids such as formic, oxalic, acetic, tartaric and citric, have no influence on the colour development. Bromide and iodide interfere and must be removed with excess of silver sulphate. As the chloride necessary for colour development is unavoidably removed in the same operation, an excess of sodium chloride must be added after the silver sulphate to give a final chloride concentration of 500–5000 ppm.

Few cations interfere; barium and lead precipitate as the sulphates on reagent addition, and must be removed previously with dilute sulphuric acid. Large amounts (10–20% in the sample) of organic solvents such as methanol, ethanol and ethyl acetate have no influence on the colour development. Chloroform does not interfere but acetone decreases the colour. Isopropanol and isobutanol inhibit the reaction

TABLE VIII.—EFFECT OF NITRITE ON NITRATE DETERMINATION AT 15°C

Taken, *ppm*		Nitrate found,	Error,
NO_3^-	NO_2^-	*ppm*	%
1	—	0·994	−0·6
1	0·1	1·003	+0·3
1	1·0	1·007	+0·7
1	10·0	1·015	+1·5

completely. No interference is caused by aliphatic amines (diethylamine), amino-alcohols (triethanolamine), amino-acids (glycine), and chelating agents (EDTA).

For drinking water, river and saline water samples, there is generally no need for preliminary preparative procedures. For sewage, polluted waters, plant tissue and soil extract, *etc.*, in which a wide variety of impurities can be present, the following procedure is recommended.

Acidify the sample with dilute sulphuric acid and add excess of permanganate. Remove the excess with oxalic acid. Note that nitrites are also oxidized in this procedure. If appreciable amounts of oxidizing agents are present, reduce them with a small excess of sulphite. Replace the cations with sodium on a suitable cation-exchange resin.

This method is useful for the determination of traces of nitrate in concentrated sulphuric acid. The following procedure is recommended.

Add to 2·5 ml of water the necessary amount of concentrated sulphuric acid to obtain a total volume of 10 ml; 1 ml of this diluted acid contains 1·5 g of sulphuric acid. Take 1 ml of 0·3% sodium chloride solution in an Erlenmeyer flask cooled in ice-water; add slowly, while stirring, the following volumes of the diluted sulphuric acid sample: 0·2 ml for "pure" (maximum nitrate admissible 0·0005%); 1 ml for "reagent" grade (0·00005%); 2 ml for "Analar" grade (0·00002%) and continue as described in the procedure, subtracting the volume of the acid sample from the reagent volume.

This simple method can be successfully used in place of the present "Standard" methods, which are less sensitive and precise. These are the diphenylamine method,[9] the indigocarmine method,[10] the ferrous sulphate methods[11,12] in which selenium interferes, and the complicated 2,4-xylenol method.[11] Selenium (50 ppm) does not affect the method described here.

Table IX shows that the method described is the most sensitive of the standard or commonly used colorimetric methods for nitrate determination. The reagent is simple to prepare and use, and the few interfering substances are easily removed.

The test can be made more rapid by keeping the reaction mixture in ice-water for only 15 min, then keeping it at 40 ± 2° for 15–20 min and reading the absorbance. A standard solution is run simultaneously.

The approximate nitrate content of a sample can easily be estimated visually. Make two comparison solutions by adding 1 and 2 drops of 0·1% alcoholic thymolphthalein solution to 10 ml of 1*M* sodium hydroxide. Working at room temperature, add sufficient chloride to the sample solution and add 1 and 2 drops of it to two 2-ml portions of reagent, and mix. Compare the sample colours with those of 2 ml of the comparison solutions. A match of the 1-drop colours after 5 min indicates about 10 ppm of nitrate, and after 15 min about 5 ppm. A match of the 1-drop sample with the 2-drop comparison solution after 5 min indicates about 20 ppm, and match of the 2-drop sample with the 1-drop comparison solution after 15 min indicates about 2 ppm. If colour development is too rapid the sample can be diluted.

TABLE IX.—COMPARISON OF METHODS

Reagent	Sensitivity,* μg N	Recovery, %	Time needed, min	Colour stability, min	Range for Beer's law, μg
Brucine[13,14]	10		20	>120	none
Chromotropic acid[15]	0·5	97	20		1–10
Diphenylamine[9,16]	0·5–0·6		20		none
Iron(II) sulphate[11,12]	190		20		
Indigo carmine[10]	4		10		none
Phenyldisulphonic acid[2]	40	90	60	>120	40–200
Phenyldisulphonic acid[17]	10		60	>120	10–50
Sodium salicylate[2]	20	90–95	60	>60	20–100
2,4-Xylenol[11]	10	90–97	120		
2,4-Xylenol[17]	25		120		25–250
3,4-Xylenol[15,16]	100		120		100–350
2,6-Xylenol[18]	2·5†	95	45	120	2·5–200?
p-Diaminodiphenylsulphone‡	7	96	20	>120	7–65
Diphenylamine–*p*-diamino-diphenylsulphone‡ at					
15°C	0·05	97–99	150	120	0·05–0·4
20–30°C	0·1	97–99	90–120	90–120	0·06–0·6
40 ± 2°C	0·1	95	40	30	0·1–0·6

* Amount needed to give an absorbance of 0·1 in a 1-cm cell.
† Read at 304 mμ.
‡ This paper.

Résumé—On utilise la *p*-diaminodiphénylsulfone dans une nouvelle méthode spectrophotométrique de dosage du nitrate. On donne les facteurs affectant le développement de la coloration. Le domaine utile pour une cellule de 1 cm est de 30–300 mg/1. Dans ce domaine, les solutions colorées sont stables et suivent la loi de Beer. La méthode est rapide et précise et elle est applicable à l'analyse de routine d'échantillons contenant des macroquantités de nitrates. Pour le dosage de microquantités de nitrate on modifie le réactif par addition de diphénylamine. La limite de dosage est alors de 0,25 mg/1 à 15°. On peut considérer cette méthode comme spécifique pour le nitrate et elle est applicable en présence de nitrite.

Zusammenfassung—p-Diaminodiphenylsulfon wird in einer neuen spektrophotometrischen Methode zur Nitratbestimmung verwendet. Die die Farbentwicklung beeinflussenden Faktoren werden angegeben. Der nutzbare Bereich für 1-cm-Küvetten liegt bei 30–300 mg/l. In diesem Bereich sind die farbigen Lösungen stabil und folgen dem Beerschen Gesetz. Die Methode ist schnell und genau und läßt sich auf die Routineanalyse von Proben anwenden, die Makromengen Nitrate enthalten. Zur Bestimmung von Mikromengen Nitrat wird das Reagens durch Zusatz von Diphenylamin modifiziert. Die Nachweisgrenze ist dann 0,25 mg/l bei 15°. Die Methode kann als spezifisch für Nitrat angesehen und in Gegenwart von Nitrit angewandt werden.

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RADIOCHEMICAL SEPARATION OF STRONTIUM BY ISOTOPIC EXCHANGE

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Summary—Isotopic exchange has been used for the rapid separation of minute quantities of radio-strontium. A number of variables such as agitation time, concentration of strontium in both phases, mode of preparation and aging of the precipitates, were studied and optimized. With an optimized procedure, exchange yields of 96% and 94% respectively were obtained when strontium sulphate and strontium oxalate precipitates were used for the exchange. Decontamination studies made with radioactive tracers of 15 elements showed that the sulphate precipitate is more selective than the oxalate, most of the elements showing <1% contamination except ^{140}Ba–^{140}La and ^{110}Ag which show high contamination. This simple procedure has also been applied for the determination of radioactive strontium in rain-water samples.

FOR many years the principle of isotopic exchange has been used in the preparation of radioactively labelled compounds and in studies on the aging of precipitates. It can also be used for devising new rapid radiochemical separation procedures, especially by isotopic exchange between an insoluble compound of an element and its ions in aqueous solution.[1–5] In the present study this technique has been applied to the separation of minute quantities of radioactive strontium from aqueous solutions.

When freshly prepared strontium sulphate and strontium oxalate precipitates are agitated in solutions containing radioactive strontium ions, a rapid isotopic exchange of strontium takes place, and in a short time most of the radioactivity is incorporated into the precipitate. A high exchange is possible only when the concentration of inactive strontium is much greater in the precipitate than in the solution, and the precipitate has low solubility. Under such conditions the very favourable equilibrium exchange ratio forms the basis of a single-step procedure for the separation of small amounts of radioactive strontium.

EXPERIMENTAL

Apparatus

Flint glass, 1-oz, square-bottomed narrow-mouth bottles with polyethylene screw caps were used in a thermostatically controlled tank to agitate the precipitate during separation. They were clamped in a mechanical shaker (Wrist-Action Shaker, Burrell Corp; Pittsburg, Pa., U.S.A.) to which a 9-in. extension arm was connected to give additional radial action.

Gamma-ray measurements were made with a Baird Atomic Model-810 Scintillation Well-Counter, and beta-activity was measured with a Tracerlab Geiger tube TGC-1. Low-level beta-measurements were made in a Nuclear-Chicago Spectroshield low background counting system with a "micromil window" and having a 40% counting efficiency for ^{90}Sr. In this system an anti-coincidence circuit was used.

Reagents

All non-radioactive chemicals used were of C.P. or analysed grade. All radioisotopes used as tracers were obtained from the Radiochemical Centre, Amersham, England, and from the Union Carbide Nuclear Company, Oak Ridge, Tenn; U.S.A. Strontium-90 free from yttrium-90 was prepared[6] by extracting ^{90}Y into 2 ml of 0·1*M* dibutylphosphate solution in chloroform from 2 ml of

equilibrium solution of ^{90}Sr–^{90}Y in 0·1*M* nitric acid. Pure carrier-free ^{90}Sr tracer remains in the aqueous layer.

Preparation of strontium sulphate and strontium oxalate

Acidify 150 ml of 3% strontium chloride solution with 2 ml of 0·5*M* hydrochloric acid and add 200 ml of 0·1*M* sulphuric acid in small portions with stirring. Allow the precipitate to stand in the mother liquor for 30 min. Separate the precipitate and wash it thoroughly by decantation with deionized water, filter it off and then dry it in an oven at 60° for 30 min. Prepare strontium oxalate similarly with 100 ml of 5% strontium chloride solution and 200 ml of 0·5*M* oxalic acid.

Isotopic exchange procedure

Take 5 ml of 0·5*M* sulphuric acid in a bottle and add strontium-85 tracer (10^4–10^5 cpm) for yield and interference studies. For contamination studies add radioactive tracers (10^5–10^6 cpm) of the contaminating ions and 1 μg of inactive strontium. Shake well to ensure thorough mixing and take out 500 μl for counting. Add 300 mg of freshly prepared strontium sulphate and shake mechanically for 10 min. Transfer the precipitate to a centrifuge cone and centrifuge at top speed for 30–60 sec. Remove the supernatant liquid, transfer the precipitate to another cone, wash it twice with water and then count it in a scintillation well-counter.

In experiments with strontium oxalate use 300 mg of the precipitate and 0·5*M* oxalic acid as exchange medium.

For the determination of radio-strontium in rain-water, evaporate 500 ml of the sample to dryness in a beaker. Wash the sides of the beaker with deionized water and evaporate to dryness again. Take up the residue in 6 ml of 0·5*M* sulphuric acid and transfer it to a bottle. Rinse the beaker twice with 3-ml portions of 0·5*M* sulphuric acid and add the rinsings to the sample bottle. Perform the exchange as above. Centrifuge and wash the precipitate, transfer it to a filter paper, and count it in a low-level beta-counter.

DISCUSSION AND RESULTS

In preliminary experiments strontium sulphate and oxalate were agitated separately for 10 min in various exchange media containing radioactive strontium tracer. The results are shown in Table I. Exchange was best with media containing the anions of the precipitate, and increased with increasing concentration of the exchange medium,

TABLE I.—DEPENDENCE OF STRONTIUM YIELD ON EXCHANGE MEDIUM AT 30°C

Substance	Concentration, *M*	% Exchange* with 200 mg of	
		$SrSO_4$	SrC_2O_4
$NaNO_3$	0·5	6·9	54·9
NaCl	0·5	16·1	51·3
Na_2SO_4	0·5	53·2	84·6
NaOH	0·5	92·1	73·6
HCl	0·5	34·3	—
HNO_3	0·5	21·9	—
H_2SO_4	0·01	64·1	—
H_2SO_4	0·1	82·3	—
H_2SO_4	0·5	95	—
H_2SO_4	1·0	96	—
$H_2C_2O_4$	0·01	—	42·8
$H_2C_2O_4$	0·1	—	69·4
$H_2C_2O_4$	0·5	4·2	93
$H_2C_2O_4$	1·0	—	93·5

* Average of triplicate runs. The standard deviation ranges from 1·8 to 2·9.

probably because of reduction in solubility by the common ion effect, and best yields were obtained with 0·5*M* solutions, which were therefore used for further studies.

The isotopic exchange reaction follows an exponential law and the progress of the reaction may be followed with the help of McKay's equation[7]

$$K = \frac{ab \ln(1 - F)}{(a + b)t}$$

where K is the rate constant in mole/sec, a and b are the concentrations of the reactants in each of the two phases (in mole/l) and F is the ratio of the quantity exchanged at time t to that exchanged at equilibrium. Since the rate of the exchange reaction is dependent on the time of contact and the concentrations of strontium in the two phases, it is necessary to study these parameters in order to develop an optimum separation procedure.

The exchange yield increases exponentially with the contact time. In the sulphate system, it increases gradually from 52% in 1 min to 96% in 10 min and then begins to level off, whereas in the oxalate system it increases rapidly from 14% in 1 min to 95% in 12 min and then levels off. In both systems equilibrium is reached after 25 min, giving a maximum exchange yield of 99%. In the optimum procedure agitation times of 10 and 12 min respectively were used for the sulphate and oxalate systems.

The recovery of strontium tracer was studied with different amounts of precipitate. With 50, 100, 200, 300 and 400 mg of precipitate, a fixed aqueous concentration of strontium, and 10 min of agitation, corresponding exchange yields of 73, 89, 95, 96 and 96% were obtained in the sulphate system, and 61, 74, 93, 94 and 94% for the oxalate system. Therefore 300 mg of precipitate was chosen as the optimum quantity for both systems.

When 300 mg of strontium sulphate was shaken with various aqueous concentrations of strontium it was found that with an aqueous concentration of strontium >40 μg/ml the exchange yield decreased slightly, and with >80 μg/ml the solution became slightly turbid with strontium sulphate. To get the best yield the solution should contain less than 40 μg of strontium per ml.

The exchange yield is also dependent on the volume of solution. It decreases as the volume increases above 10 ml, falling by 17% when the aqueous volume is 25 ml, but this decrease can be compensated by increasing the amount of precipitate to 1 g.

Adsorption plays an important role in this type of heterogeneous isotopic exchange reaction. Therefore, the mode of preparation and the aging of the precipitate may affect the exchange if they produce changes in the surface area of the precipitate. Strontium sulphate prepared from 0·005–0·01*M* solutions gave ~10% lower exchange yield than that prepared from 0·1–0·5*M* solutions, possibly because the crystals obtained from the more dilute solutions may have been more uniform and regular in shape, with a smaller total surface area available for exchange.

Aging of the precipitate in the mother liquor also decreases the exchange yield. Aging for 5 hr gave a 15% decrease in exchange yield, and washing the precipitate with ethyl alcohol decreased the exchange yield by 17%. Thermal aging of the precipitate at 300° for 1 hr decreased the yield by 25%, probably by growth of particle size. Aging for 4 hr gave no further decrease in the yield, but raising the aging temperature to 500° further decreased the yield.

Interferences

Hydrochloric, hydrobromic and nitric acids below 1*M* concentration do not affect the yield in the sulphate system. Oxalic, tartaric and citric acids below 0·1*M* concentration have no effect on the yield either but increasing the concentration of these acids decreases the yield rapidly. Sulphites, phosphates and phosphoric acid also decrease the yield when present in concentrations above 0·05*M*.

Since mineral acids attack strontium oxalate, they decrease the yield considerably in the oxalate system, even at concentrations of 0·1*M*, and must be neutralized before the exchange step for the best yield to be obtained. Elements which would precipitate during neutralization must be removed first. Sulphites, phosphates, tartaric acid and citric acid in concentration above 0·05*M* also decrease the yield.

Decontamination

Decontamination studies were made for both systems to check the selectivity of the procedure. Radioactive tracers (with their daughters) of 15 elements, representative of various parts of the Periodic Table, were used. The results are summarized in Table II. In most cases the contamination was less than 1%. Silver and Ba–La

TABLE II.—SEPARATION OF STRONTIUM AND CONTAMINANTS IN THE ISOTOPIC EXCHANGE PROCEDURE AT 30°C

Tracer	Weight* μg	% Separated†	
		$SrSO_4$–H_2SO_4 system	SrC_2O_4–$H_2C_2O_4$ system
^{65}Zn	C.F.	0·01	0·27
^{90}Y	C.F.	0·44	0·8
^{90}Y	10	0·02	0·18
^{60}Co	0·1	0·03	0·74
^{115}Cd	173	0·06	5·7
^{124}Sb	0·3	0·08	0·98
^{144}Ce–^{144}Pr	435	0·14	0·33
^{137}Cs	21	0·19	0·46
^{114}In	2·7	0·38	6·58
^{131}I	C.F.	0·61	0·92
^{203}Hg	18·1	0·67	2·3
^{106}Ru–^{106}Rh	1·3	0·69	1·8
^{192}Ir	1·6	1·9	1·8
^{95}Zr–^{95}Nb	11·7	2·1	4·4
^{110}Ag	2·3	11·1	23·1
^{110}Ag	1000	7·4	15·7
^{140}Ba–^{140}La	1·6	93·8	90·2
^{85}Sr	0·9	96 ± 1·9	94·2 ± 2·1

* Weight of inactive element present before separation; C.F. means carrier-free.

† Average of duplicate runs, except for strontium which is average of 7 runs, the error quoted being the standard deviation.

showed high contamination. Contamination by silver is probably due to adsorption of its ions on the precipitate, which can be reduced considerably by adding 1 mg of silver carrier. Since barium behaves similarly to strontium but forms a less soluble sulphate and oxalate, it exchanges with strontium in the precipitates, and shows very high contamination. Therefore, the method is not useful when

the sample contains radioactive barium and calcium. From the decontamination data, it can be seen that the sulphate system is the more selective.

The simple isotopic exchange procedure was applied for the separation of radio strontium from fall-out rain-water samples. Chemical recovery of strontium was determined to be 94 ± 2% by adding a known amount of strontium tracer to 590-ml samples of deionized water and carrying out the separation as described for rain-water samples. Rain-water samples, collected during the months of March, July and September, 1966 by the Health Physics Division of the Atomic Energy Centre, Lahore, were analysed for radio-strontium by this procedure. The measurement of beta-emitting ^{90}Sr is considerably affected by self-absorption in the precipitate (which weighs ~78 mg/cm²) and corrections must be applied to the observed count. Gross beta-activity of the samples was also determined by evaporating a total of 25 ml in 1-ml portions on a planchet. The results are summarized in Table III.

TABLE III.—DETERMINATION OF RADIO-STRONTIUM IN RAIN-WATER SAMPLES

Sample	Corrected nett count, *cpm*	Amount of radio-strontium, 10^{-8} *μC/ml*	Average of duplicate runs, 10^{-8} *μC/ml*	Gross activity, 10^{-8} *μC/ml* (average of duplicate runs)
March 1966	3·6	0·86 ± 0·23	0·85 ± 0·23	5·4 ± 1·6
March 1966	3·5	0·84 ± 0·22		
July 1966	7·2	1·72 ± 0·32	1·7 ± 0·32	9·9 ± 2·1
July 1966	7·0	1·68 ± 0·32		
Sept. 1966	6·3	1·51 ± 0·3	1·54 ± 0·31	9·4 ± 1·9
Sept. 1966	6·6	1·58 ± 0·31		

All samples were counted for 80 min each. Background of the counter was 1·1 cpm. The error quoted is the error due to the counting statistics.

The isotopic exchange technique for the separation of trace amounts of radioactive strontium is rapid and fairly selective. The simple procedure gives a high chemical yield and does not require special equipment. The technique can be easily applied to samples such as rain-water.

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Zusammenfassung—Zur schnellen Abtrennung kleiner Mengen Radiostrontium wurde der Isotopenaustausch verwendet. Eine Anzahl von Variablen wie Schüttelzeit, Konzentration von Strontium in beiden Phasen sowie Art der Herstellung und Alterung der Niederschlage wurden untersucht und optimiert. Mit einer optimierten Vorschrift wurden Austausch-Ausbeuten von 96 und 94% mit Strontiumsulfat bzw. Strontiumoxalatniederschlägen beim Austausch erhalten. Dekontaminationsuntersuchungen mit radioaktiven Tracern von 15 Elementen zeigten, daß der Sulfatniederschlag selektiver ist als das Oxalat, wobei die meisten Elemente unter 1% Kontamination zeigen, außer ^{140}Ba, ^{140}La und ^{110}Ag, die hohe Kontamination zeigen. Dieses einfache Verfahren wurde auch auf die Bestimmung von Radiostrontium in Regenwasserproben angewandt.

Résumé—On a utilisé l'échange isotopique pour la séparation rapide de faibles quantités de radio-strontium. On a étudié et rendu optimales un certain nombre de variables comme le temps d'agitation, la concentration du strontium dans les deux phases, le mode de préparation et de vieillissement des précipités. Avec la technique rendue optimale, on a obtenu des rendements d'échange de 96% et 94% respectivement quand les précipités de sulfate de strontium et d'oxalate de strontium ont été utilisés pour l'échange. Des études de décontamination effectuées avec les traceurs radioactifs de 15 éléments ont montré que le précipité de sulfate est plus sélectif que celui d'oxalate, la majeure partie des éléments montrant une contamination <1% à l'exception de ^{140}Ba, ^{140}La et ^{110}Ag qui montrent une contamination élevée. On a aussi appliqué cette technique simple au dosage du strontium radioactif dans des échantillons d'eau de pluie.

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DETERMINATION OF SELENIUM AND TELLURIUM IN SILVER CHLORIDE AND URANIUM OXIDE

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Summary—Methods are described for the determination of selenium and tellurium in crude silver chloride produced as a by-product of the refining of gold, and in high-purity uranium oxide. Selenium and tellurium are separated from one another as well as from the numerous other substances in the sample before they are extracted into organic solvents and determined spectrophotometrically. For the determination of selenium 3,3′-diaminobenzidine is used and for tellurium, *sym*-diphenylthiourea. A minimum of 2 ppm of each element may be determined in silver chloride and 0·3 ppm in uranium oxide. Statistical data are given to show the precision and accuracy of the methods.

SILVER compounds of high purity are often specified for photographic and other industrial purposes, and it is proposed to prepare them from the crude silver chloride produced as a by-product of South African gold. At the outset it is necessary to be able to analyse the crude material as well as the refined products. Selenium and tellurium are two particularly undesirable elements in silver compounds, and the uranium oxide used for making nuclear fuels must also be of high purity and containing as little as possible of these two elements. The work covered in this paper was prompted by the lack of published analytical procedures for small amounts of the elements in these types of material.

The selenium and tellurium are assumed to occur as minute inclusions of selenide and telluride. Many elements interfere in the methods that have been proposed for the determination of selenium and tellurium, so that a fairly complete separation of the two elements from the impurities and from each other is necessary. Schoeller and Powell[1] suggest roasting in a stream of dry chlorine gas as a means of separating selenium and tellurium from silver, but the present investigators were unsuccessful in applying this technique. Spectrographic methods lack the necessary sensitivity, especially for selenium; polarographic methods require the isolation of the two elements. Spectrophotometric methods appear to be the most applicable.

The best spectrophotometric procedures for the determination of selenium depend upon the formation of the compound piazselenol, which has an intense yellow colour and is extractable into organic solvents. The most frequently used reagents for the formation of piazselenol are 2,3′-diaminonaphthalene and 3,3′-diaminobenzidine. The former reagent was investigated by Lott[2] but the method lacks reproducibility. Hoste,[3] and Hoste and Gillis[4] originally applied 3,3′-diaminobenzidine to selenium determinations, and showed it to be a selective and moderately sensitive reagent. Cheng[5] investigated the reagent in detail and proposed a modified procedure in which small amounts of most of the elements do not interfere.

The only reagents for tellurium that appear to possess the necessary sensitivity are bismuthiol(II) and *sym*-diphenylthiourea. The former was investigated by Jankowsky and Ksir,[6] but we were unable to obtain reproducible results with their method. The results obtained with *sym*-diphenylthiourea, as proposed by Yoshidu and Hikime,[7] are reproducible and relatively sensitive, though many substances interfere and necessitate the separation of the tellurium.

EXPERIMENTAL

Reagents

All reagents should be of the highest purity obtainable.

Sodium peroxide, +20 mesh.

Sodium nitrate wash solution. Dissolve 20 g of sodium nitrate in water and dilute to 1 l. Adjust the pH value to 8·5 by means of 5% sodium hydroxide solution.

Nitric acid, 50% v/v, and 1% v/v.

Aluminium nitrate solution. Dissolve 69·53 g of $Al(NO_3)_3.9H_2O$ in water containing 5 ml of nitric acid, and dilute to 100 ml; 1 ml ≡ 50 mg of aluminium.

Methyl Red, aqueous solution, 0·2% *w/v.*

Ammonium chloride, solution, 1% *w/v.*

Sodium carbonate–bicarbonate solution. Dissolve 50 g of sodium carbonate and 50 g of sodium bicarbonate in water and dilute to 500 ml.

Formic acid, 2·5M solution. Dilute 11·5 ml of formic acid to 100 ml with water.

3,3′-Diaminobenzidine solution, 0·5% *w/v.* Dissolve 0·125 g of 3,3′-diaminobenzidine tetrahydrochloride in water and dilute to 25 ml. Prepare just before use.

Sodium hydroxide, 2M.

Standard selenium solution. Transfer 0·2000 g of selenium powder to a 125-ml Phillips beaker. Add 15 ml of nitric acid and heat until dissolved. Dilute to 1 l. in a volumetric flask. The selenium is in the quadrivalent state. For use dilute 10 ml to 200 ml; prepare fresh weekly.

Iron(III) nitrate solution. Dissolve 73·5 g of $Fe(NO_3)_3.9H_2O$ in water containing 5 ml of nitric acid and dilute to 100 ml; 1 ml ≡ 100 mg of iron.

Ammonium nitrate wash solution. Neutralize 100 ml of nitric acid with aqueous ammonia and dilute to 1500 ml with water. Adjust the pH value to approximately 8.

Cation-exchange resin. Dowex 50W–8X (50–100 mesh).

Sym-*Diphenylthiourea solution,* 1% *w/v.* Dissolve 2 g of *sym*-diphenylthiourea in approximately 100 ml of chloroform and dilute to 200 ml with chloroform. Prepare fresh monthly.

Standard tellurium solution. Dissolve 0·8999 g of telluric acid ($H_2TeO_4.2H_2O$) in 100 ml of water, add 10 ml of hydrochloric acid and dilute to 500 ml. The tellurium is in the sexivalent state; 1 ml ≡ 1 mg of tellurium. For use dilute 5 ml to 1 l.; prepare fresh daily.

Procedure

Dissolution of uranium oxide sample. Dissolve 5 g of the sample in a mixture of 9 ml of nitric acid and 1 ml of hydrochloric acid, and evaporate to a moist state. Add 1 ml of iron(III) nitrate solution and about 200 ml of water. Heat to about 60°, and add hot sodium carbonate–bicarbonate solution until the uranium is all complexed and the iron precipitated, then add 10 ml in excess. Filter off the precipitate on a Whatman No. 541 filter paper and wash once with hot 2% sodium bicarbonate solution. Dissolve the precipitate in a minimum of hot 50% nitric acid and repeat the precipitation with the sodium carbonate–bicarbonate solution. Dissolve the precipitate in 20 ml of hot 50% nitric acid. Add 0·6 g of silver nitrate, dilute to 250 ml, and add 8 g of sodium peroxide. Continue as described for silver chloride after the leaching of the fusion.

Dissolution of silver chloride sample. Transfer the sample (not exceeding 1 g) to a nickel crucible of suitable capacity. Add 5 g of sodium peroxide, mix, and fuse over a low flame until all the sample is decomposed. Cool the fusion, leach it in 250 ml of water, and adjust the pH value to 8·5 with dilute nitric acid (Note 1). Boil for 20 min to decompose the peroxides. Dilute with boiling water to approximately 350 ml, add 1 g of paper pulp and stir. Allow the precipitate to settle for 1 or 2 min, and filter it off on a Whatman No. 541 filter paper, decanting off the supernatant liquid before transferring the precipitate. Wash with hot sodium nitrate wash solution until the precipitate is free from chloride. Ten washes are normally sufficient.

Selenium is determined in the filtrate and tellurium in the precipitate.

Determination of selenium. Evaporate the filtrate to approximately 20 ml, neutralize it with hydrochloric acid, and add 30 ml in excess. Adjust the volume to 70 ml and boil gently for 2 min. Dilute

to 250 ml and add 1·5 ml of aluminium nitrate solution. Heat to approximately 80°, and add 2 drops of Methyl Red solution and aqueous ammonia until the indicator colour just changes to yellow. Boil for 2 min, and immediately filter off the precipitate on a 12·5-cm Whatman No. 541 filter paper, and wash it four times with hot ammonium chloride wash solution. Sluice the precipitate back into the original beaker, and dissolve the remaining traces off the paper with hot 50% nitric acid. Add 1 ml of 2*M* sodium hydroxide, and evaporate the solution to a moist state (Note 2).

Add 3·5 g of tartaric acid and 10 ml of water. Rotate the beaker until the salts are dissolved, and transfer the solution to a 150-ml beaker that has been marked at the 40-ml level. The volume must not exceed 30 ml at this stage. Add 2 ml of 2·5*M* formic acid, and, with aqueous ammonia checking it with a pH-meter, adjust the pH value to between 2 and 2·5. Adjust the volume to 40 ml. Add 2 ml of 3,3′-diaminobenzidine solution, mix, and allow to stand for 45 min.

Adjust the pH value to 6·5 with ammonia (check with a pH-meter). Transfer the solution to a 125-ml separating funnel that has been previously marked at the 50-ml level, and adjust the volume to 50 ml. Add 10 (±0·01) ml of toluene and shake for 2 min. Allow 5 min for the phases to separate, and discard the aqueous solution. Filter the organic phase through dry, double, 7-cm Whatman No. 541 filter paper into a 50-ml beaker. Cover it with aluminium foil to prevent evaporation. Within 1 hr read the transmittance at 420 mμ on a spectrophotometer against a reference blank treated in the same way as the sample.

Prepare a calibration curve by adding portions of the diluted standard selenium solution containing 5, 10, 15, and 20 μg of selenium to 0·5 g portions of selenium-free silver chloride in nickel crucibles. Add a pellet of sodium hydroxide, and evaporate to dryness in an oven at 110°. Continue as described in the procedure (Note 3).

Determination of tellurium. The tellurium is quantitatively held in the precipitate obtained as described under "Dissolution of sample". Dissolve the precipitate through the paper, using a jet of hot 50% nitric acid from a wash bottle. Wash the paper with hot 1% nitric acid to give a total volume of 200 ml. Add 1 ml of iron(III) nitrate solution and heat the solution to approximately 85°. Precipitate the iron with aqueous ammonia, and adjust the pH to approximately 8. Filter off hot on a Whatman No. 541 filter paper without washing. Sluice the precipitate back into the original beaker, and wash the paper with 20 ml of hot 50% nitric acid and then hot water to give a total volume of 150 ml. Repeat the precipitation as described above but wash with five 20-ml portions of hot ammonium nitrate was solution (Note 4). Sluice the precipitate back into the original beaker with a minimum of water, and dissolve the last traces from the paper with hot 50% nitric acid. Evaporate the solution to 2 ml, and then dilute to 100 ml. Wear goggles when using hot nitric acid.

Place a small wad of glass wool at the base of a 50-ml burette, wash in 15-ml of resin, and condition the resin with 50 ml of 50% nitric acid at a flow-rate of 1 drop/sec. Wash the column free from acid. Pass the sample through the column at a rate of 1 drop/sec, and wash the column 5 times with 15-ml portions of water. To the eluate, add 5·5 ml of perchloric acid and 5 ml of hydrochloric acid, and evaporate to fumes. Transfer the material so obtained to a 125-ml Phillip's beaker, using a minimum amount of water. Add 2 ml of hydrochloric acid, evaporate to fumes, and fume for 1 min (Note 5). Transfer to a 50-ml separating funnel previously marked at the 10·5-ml level, and dilute to 10·5 ml. Add 10 (±0·01) ml of *sym*-diphenylthiourea solution, and shake for 1 min. Allow 10 min for the solutions to separate, and collect the organic phase in a 50-ml beaker containing 0·5 g of anhydrous sodium sulphate. Cover it with aluminium foil. Read the transmittance at 380 mμ on a spectrophotometer against a reference blank prepared by adding 5·5 ml of perchloric acid and 2 ml of hydrochloric acid to a 125-ml Phillip's beaker, fuming, and extracting as described above.

Prepare a calibration curve by adding portions of tellurium solution containing 5, 10, 15, 20, and 25 μg of the element to 0·5 g portions of tellurium-free silver chloride in nickel crucibles, and add a pellet of sodium hydroxide. Evaporate to dryness in an oven at 110° and follow the procedure described. Plot a calibration graph.

Notes

1. This step should be carried out as quickly as possible because the highly alkaline solution dissolves silica from the beaker and makes subsequent filtration difficult.

2. The addition of a sodium salt prevents the volatilization of selenium that otherwise occurs when hydrochloric acid solutions are evaporated. To prevent a loss of selenium, the residue must not be allowed to become dry.

3. Because small losses of selenium occur in the procedure, it is necessary to prepare the calibration graph by carrying standard samples through the entire procedure.

4. To prevent tellurium from passing into the filtrate, it is essential to wash with a solution that approximates as closely as possible to the sample solution.

5. The hydrochloric acid reduces tellurium to the quadrivalent state, but prolonged fuming with perchloric acid causes re-oxidation.

DISCUSSION

Dissolution of the sample

Samples of uranium oxide were dissolved in nitric acid and a little hydrochloric acid was added to reduce the selenium and tellurium to the quadrivalent state for precipitation with sodium carbonate; iron was added as a carrier. The addition of sodium peroxide to the redissolved precipitate is necessary to oxidize the selenium and tellurium to the sexivalent state for the separation of the two elements; the presence of silver and iron is necessary for a complete separation.

Because silver chloride is insoluble in acidic solutions, any operations in an acid medium required the previous complete separation of the silver from the chloride. Also, because selenium interferes in the spectrophotometric methods for tellurium, the separation of the two elements is of the utmost importance.

Fusions with sodium carbonate, sodium hydroxide, and sodium peroxide were investigated, the last-named proving to be by far the most satisfactory. One g of the sample was dissolved in 5 g of sodium peroxide in a nickel crucible. After a water leach, the precipitate of silver and nickel occluded the tellurium, whereas the selenium passed into the filtrate. Hydrogen peroxide was decomposed by boiling, though it was necessary to partially neutralize the solution first. At the reduced alkalinity, the precipitate settled more rapidly, and the dissolution of silica from the beaker, which rendered subsequent filtration difficult, was prevented. Most of the metallic impurities, including the silver, accompanied the tellurium, whereas the chloride remained in solution with the selenium. When the sample was dissolved by sintering with sodium peroxide in a platinum crucible and leaching with water, not all of the tellurium was collected in the precipitate. This indicates that silver alone is not an effective collector for tellurium. When a nickel crucible was used, a complete separation of selenium and tellurium was obtained, and the nickel was easily separated in subsequent operations. Selenium recoveries were checked by the addition of the radioactive isotope (^{75}Se) to the fusion mixture and measurement of the activity of the filtrate, which was found to contain virtually all the selenium. No suitable tellurium isotope was available, so the tellurium recovery was assessed on the results obtained with the whole procedure and by the absence of tellurium in the filtrate.

Determination of selenium

Reduction of sexivalent selenium. Selenium is precipitated by ammonia in the presence of aluminium only if it is in the quadrivalent state; it must also be in the quadrivalent state before it will react with 3,3′-diaminobenzidine. The element is present in the oxidized state after fusion with sodium peroxide, and it was therefore necessary to find a suitable reducing agent. Formaldehyde, iron(II) ammonium sulphate, hydrazine, sulphur dioxide, and ascorbic acid were tried, but they either interfered in the later stages of the method or reduced the selenium to the element. Boiling the sample for 2 min in 4*M* hydrochloric acid was found to effectively reduce the selenium without loss, though conflicting reports appear in the literature on the volatility of selenium in boiling hydrochloric acid solutions. This point was settled by the use of seven 50-μg portions of selenium; the mean recovery was 49·7($\pm$0·5) μg.

Precipitation of selenium with aluminium hydroxide. The large amount of sodium salts present in the solution prevents evaporation to the low volume necessary for the

colour development stage of the method and thus requires separation. Iron(III) hydroxide has been used as a carrier for both selenium and tellurium,[8,9] but the precipitation of selenium was found to be incomplete in both the (IV) and (VI) oxidation states; also, iron is an undesirable element in the colour development stage of the method. The precipitation of quadrivalent selenium with ammonia in the presence of aluminium was found to be quantitative, and the precipitate can be washed at pH 5 with ammonium nitrate solution without loss of selenium. This was tested by precipitating six 20-μg portions of selenium on aluminium hydroxide as described. The recovery was 19·8($\pm$0·2) μg, whether the precipitate was washed or not.

TABLE I.—EFFECT OF TARTARIC ACID ON THE FORMATION OF PIAZSELENOL IN THE PRESENCE OF ALUMINIUM

Tartaric acid added, *g*	Selenium recovered, μg
1·0	42·4
1·5	44·8
2·0	45·8
3·0	49·4
3·5	50·6
4·0	50·8

The solution contained 50 μg of selenium and 75 mg of aluminium.

Dissolution of aluminium hydroxide precipitate. After the precipitation of the selenide on aluminium hydroxide, a considerable excess of acid was required to redissolve the precipitate. Neutralization of this acid was necessary to obtain the correct pH value for colour development, and the ammonium salts of nitric, sulphuric, and hydrochloric acids interfere. The difficulty was overcome by dissolving the aluminium hydroxide precipitate in nitric acid and evaporating off most of the excess of acid. Selenium was not lost during this evaporation, as has been established by other investigators.[9]

Colour development and measurement. For the spectrophotometric determination of the selenium, 3,3′-diaminobenzidine was used. The reaction depends upon the formation of the intensely yellow compound, piazselenol, formed at pH values below 4 and extracted into organic solvents above pH 5. The formation is complete in 30 min in the presence of formic acid, and may be hastened by heating, though this is not recommended because the period of heating is critical. Piazselenol has absorption maxima at wavelengths of 340 and 420 mμ, but the former is not recommended because the 3,3′-diaminobenzidine absorbs strongly at this wavelength. The experimental conditions established by Cheng[5] were adopted for the formation, extraction, and measurement of the piazselenol. As observed by other investigators,[10] variations in the colour of the extracted piazselenol are significant and account for the major portion of the standard deviation in Table IV.

Effect of tartaric acid. Aluminium, added as a co-precipitant for selenium, interfered in the formation and extraction of the piazselenol by causing emulsions to form with the extracting solvent. As reported by Cheng,[5] tartaric acid could be used to form complexes with the aluminium, but a considerable excess was necessary for a complete recovery of the selenium. This effect is illustrated in Table I.

The results were obtained by comparing the measurements with a calibration graph drawn from standards containing no aluminium or tartaric acid.

Effect of ammonium salts. The effect of ammonium salts was studied in the absence of tartaric acid by adding varying amounts of the corresponding concentrated acid to standard selenium solutions, neutralizing with ammonia, and extracting the piazselenol as described in the method. Additions of 0·5 ml of concentrated nitric, sulphuric, or hydrochloric acid resulted in a reduced extraction of selenium. Tartaric acid greatly diminished the effect of ammonium nitrate and, in the presence of 3 g or more of tartaric acid, 2 ml of nitric acid could be tolerated, as shown in Table II.

TABLE II.—EFFECT OF AMMONIUM NITRATE ON THE RECOVERY OF SELENIUM

Nitric acid (sp.gr. 1·39) added and neutralized, *ml*	Selenium recovered, *μg*	
	In the presence of tartaric acid, *μg*	In the absence of tartaric acid,
1	50·8	46·8
2	49·9	43·5
3	48·5	35·6
4	47·1	33·8
5	46·0	33·8

The solutions contained 50 μg of selenium and 75 mg of aluminium.

The experimental conditions for the selenium determination were thus established; the 75 mg of aluminium used for precipitation required 3·5 g of tartaric acid, which in turn allowed up to 2 ml of nitric acid to be present before neutralization.

Interference of cations. Cheng[5] found that in the presence of EDTA and tartaric acid 1 mg of tellurium(IV) and up to 5 mg each of chromium(III), molybdenum(VI), nickel(II), copper(II), and iron(III) did not interfere with 10 μg of selenium. If these elements are present, 10 ml of 0·1*M* EDTA may be added without altering the sensitivity of the method. Vanadium(V) (0·2 mg) also interferes, as do oxidizing agents which oxidize the 3,3′-diaminobenzidine.

Determination of tellurium

The precipitate obtained after dissolution and filtration of the fused sample contains the tellurium, the silver, and most other metallic elements present in the sample. It must be washed until free of chloride since as little as 6 mg of silver chloride co-precipitates 40% of the tellurium at the 25-μg level. Thus when the precipitate is dissolved in nitric acid, the solution must be clear.

Co-precipitation of tellurium with iron(III). As the interferences in the spectrophotometric determination of tellurium by *sym*-diphenylthiourea are numerous, it is necessary to separate the tellurium from most elements. Several investigators have reported that sexivalent tellurium is quantitatively precipitated with ammonia in the presence of iron,[11] but it is generally agreed that tellurium is lost if the precipitate is washed. The present investigators have established that if the wash solution corresponds closely to the supernatant solution after the iron has been precipitated with aqueous ammonia no losses of tellurium are incurred on washing. The precipitation of the tellurium was found to be quantitative for both the quadrivalent and sexivalent states. Analysis of solutions containing 25 μg of tellurium(IV) yielded 24·8(±0·2) μg of tellurium after precipitation as described and analysis of the precipitate; solutions of tellurium(VI) yielded 25·1(±0·4) μg of tellurium.

Two iron(III) hydroxide precipitations were carried out, but only the precipitate from the second precipitation was washed, since it was not possible to ascertain the salt concentration in the first solution closely enough to prepare an efficient wash solution at the time of the first precipitation.

Ion-exchange separation of the iron and other impurities. The amount of iron required as a "collector" for the precipitation of the tellurium with ammonia was more than could be tolerated in the colour development stage. Also other cations present in the original sample required separation. The cation-exchange resin, Dowex 5W–8X, effectively absorbed the remaining interfering cations while tellurium(VI) passed quantitatively through the column. Tellurium(IV) was sorbed on the column.

Reduction of the tellurium. All the operations carried out so far require the tellurium to be in the sexivalent state. As the reaction with *sym*-diphenylthiourea takes place only with tellurium(IV), reduction is necessary. Reducing agents such as sodium dithionite, sulphur dioxide, ascorbic acid, hydroxylamine hydrochloride, and hydrazine sulphate were unsuccessful. The addition of hydrochloric acid and evaporation to fumes with perchloric acid was found to reduce all the tellurium. It is necessary to remove all but traces of the hydrochloric acid, but prolonged fuming is undesirable because it causes re-oxidation of the tellurium. The reduction reaction is

$$H_2TeO_4 + 2HCl \rightarrow H_2TeO_3 + Cl_2 + H_2O.$$

The completeness of reduction was checked by preparation of standard solutions of tellurium(IV) and tellurium(VI). Calibration graphs for the two solutions coincided after the tellurium(VI) had been reduced with hydrochloric acid. The length of time for which the solutions could be fumed strongly before re-oxidation took place was also ascertained, as shown in Table III. One minute of strong fuming was adopted for the procedure.

TABLE III.—OXIDATION OF TELLURIUM BY FUMING PERCHLORIC ACID

Tellurium(IV) (μg) recovered after fuming strongly for					
0·5 min	1 min	3 min	5 min	10 min	30 min
29·7	29·9	28·5	27·5	22·5	3·1
29·9	30·6	29·1	26·5	20·1	9·6

The solution contained 30 μg of tellurium.

Portions of the standard tellurium(VI) solution were determined spectrophotometrically without going through the preliminary separation steps of procedure, and the results were accumulated. These results were obtained over a period of several months. A statistical analysis of these values indicates the reproducibility of this part of the method.

Number of determinations	18
Tellurium added	25·0 μg
Mean tellurium recovered	24·77 μg
Standard deviation	1·02 μg.

Extraction and spectrophotometric measurement. *sym*-Diphenylthiourea[7] is used for the spectrophotometric determination of the tellurium. Many substances interfere, but these are eliminated in the preceding separations.

Iron, bismuth, lead, and selenium are perhaps the most serious interferences and must be absent. The tellurium complex may be extracted from either hydrochloric

or perchloric acid, but the latter was chosen because it permitted the nitric acid in the sample solution to be eliminated by fuming. Maximum sensitivity is attained by measuring the complex at 380 mμ.

RESULTS

Results obtained on the crude silver chloride sample were analysed statistically for both selenium and tellurium as shown in Tables IV and V. The sample was also "spiked" with known amounts of selenium and tellurium and analysed to determine the completeness of recovery.

TABLE IV.—SELENIUM RESULTS OBTAINED ON THE SAMPLE OF CRUDE SILVER CHLORIDE

Se added, μg	Total Se recovered, μg	Nett Se recovered, μg	Mean value, μg	No. of determinations	Standard deviation, μg
0	14·6	14·6			
5	19·9	14·9	14·23	23	1·28
10	23·2	13·2			

One gram of sample was used for each determination.

TABLE V.—TELLURIUM RESULTS OBTAINED ON THE SAMPLE OF CRUDE SILVER CHLORIDE

Te added, μg	Total Te recovered, μg	Nett Te recovered, μg	No. of determinations	Standard derivation, μg
0	3·4	—	8	
5	7·8	4·5	3	
10	12·6	9·3	10	0·31
15	17·7	14·3	12	0·70
25	27·3	23·9	2	
30	34·5	31·1	2	
40	45·5	42·1	2	
50	53·4	50·0	2	

One gram of sample was used for each determination.

A sample of triuranium octaoxide was analysed for selenium and tellurium giving the results shown in Table VI. The sample was also "spiked", and a portion of the pure oxide was run concurrently as a blank. The results indicate that the selenium and tellurium content was under 0·5 ppm, and, at this low level, the "spike" recoveries were considered satisfactory.

Discussion of results

The amounts of selenium and tellurium recovered, when known amounts of these elements were added to pure silver chloride and analysed as described in the complete procedure, were low when compared with standard solutions analysed by the colour

TABLE VI.—SELENIUM AND TELLURIUM RESULTS ON A SAMPLE OF U_3O_8

	Total Se recovered, μg	"Spike" recovered, μg	Total Te recovered, μg	"Spike" recovered, μg
Pure U_3O_8	0·3		0	
Sample	0		1·9	
Sample + 2 μg each of Se and Te	2·6	2·6	3·8	1·9
Sample + 5 μg each of Se and Te	5·4	5·4	6·7	4·8

Five g of sample was used for each determination.

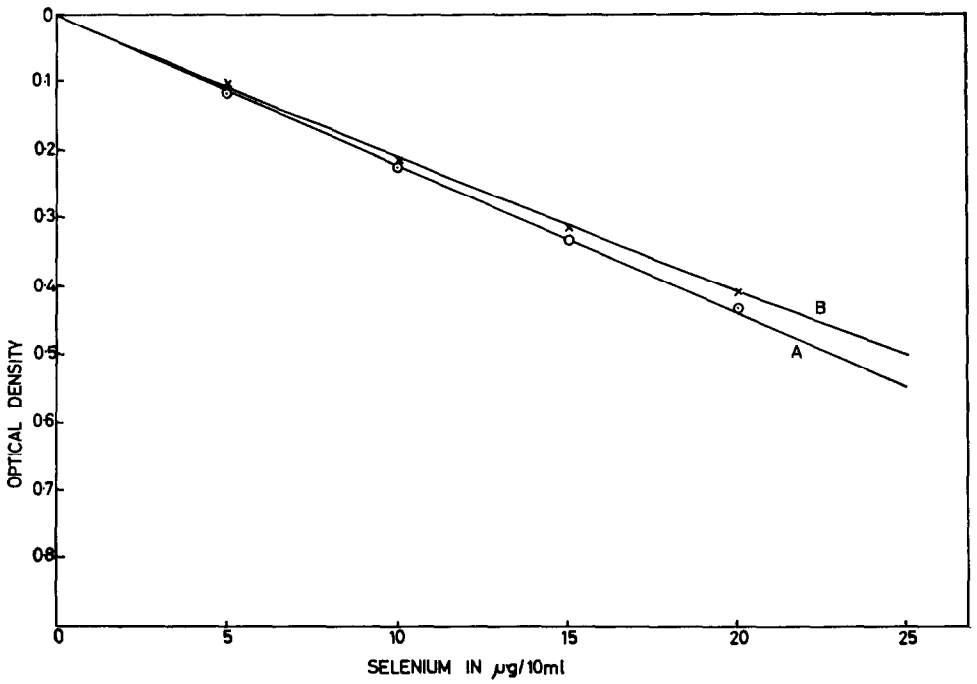

FIG. 1.—Calibration graphs for selenium determinations.
A—Prepared from standard solutions put through extraction step only;
B—Prepared from standards added to pure silver chloride and put through full procedure.

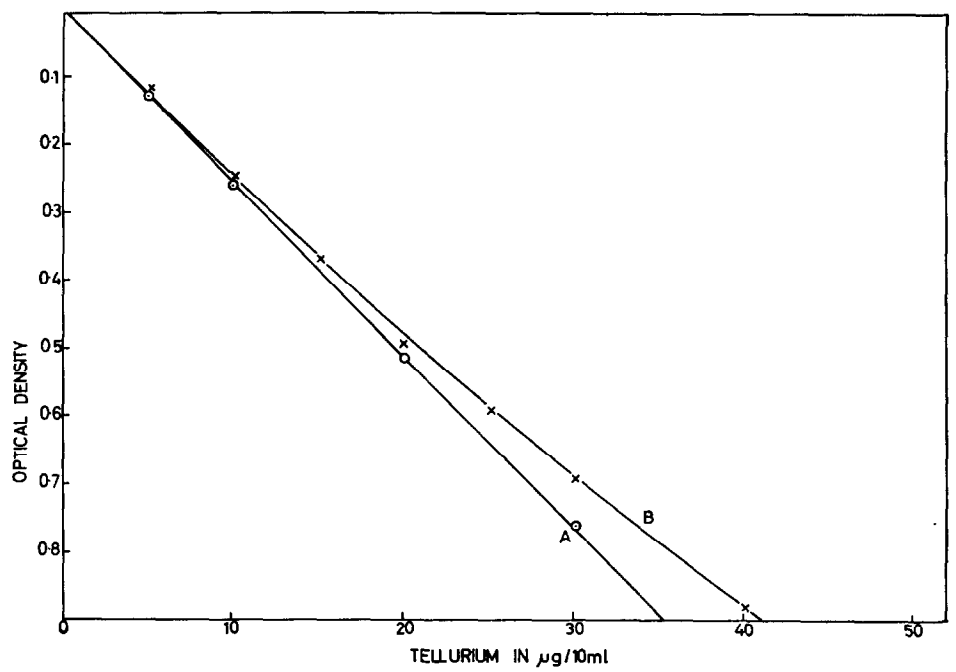

FIG. 2.—Calibration graphs for tellurium determination.
A—Prepared from standard solutions put through extraction step only;
B—Prepared from standards added to pure silver chloride and put through full procedure.

development and solvent extraction part of the procedure, *i.e.*, standards not taken through the separation procedures described in the method. When these results were plotted, the curves in Figs. 1 and 2 were obtained, indicating that losses of selenium and tellurium were incurred during the procedure and these losses increased with increasing amounts of selenium and tellurium. The authors can offer no explanation for the latter phenomenon, but the former possibly results from consistent losses, at various stages in the procedure, that were too small to be detected by the spectrophotometric procedure. The cumulative effect of these small losses may account for the low results obtained on the pure silver chloride. As the calibration graph obtained by the complete procedure was reproducible and enabled reasonably accurate results to be obtained, it was decided not to investigate these losses any further. The curved graphs could be closely reproduced by three independent operators, and the results reported for the samples were calculated by use of these calibration graphs.

With modification to the dissolution technique, the procedure is adaptable to the determination of selenium and tellurium in other silver and uranium compounds, as well as in the metals.

Acknowledgements—The authors wish to thank Dr. R. E. Robinson, Director of the National Institute for Metallurgy, for permission to publish the work described in this paper.

Zusammenfassung—Methoden zur Bestimmung von Selen und Tellur in als Nebenprodukt der Goldraffination anfallendem rohem Silberchlorid und in hochreinem Uranoxid werden beschrieben. Selen und Tellur werden voneinander und von den zahlreichen anderen Stoffen in der Probe getrennt, ehe sie in organische Lösungsmittel extrahiert und spektrophotometrisch bestimmt werden. Zur Bestimmung von Selen wird 3,3′-Diaminobenzidin verwendet, für Tellur sym-Diphenylthioharnstoff. Als Minimum konnen 2 ppm von beiden Elementen in Silberchlorid und 0,3 ppm in Uranoxid bestimmt werden. Zum Nachweis von Genauigkeit und Richtigkeit der Methode werden statistische Daten angegeben.

Résumé—On décrit des méthodes de dosage du sélénium et du tellurium dans le chlorure d'argent brut obtenu comme sous-produit du raffinage de l'or et dans l'oxyde d'uranium de haute pureté. On sépare le sélénium et le tellurium l'un de l'autre ainsi que de nombreuses autres substances dans l'échantillon avant de les extraire en solvants organiques et de les doser spectrophotométriquement. Pour le dosage du sélénium, on utilise la 3,3′-diaminobenzidine et pour le tellurium la diphénylthiourée symétrique. On peut doser un minimum de 2 p.p.m. de chaque élément dans le chlorure d'argent et 0,3 p.p.m. dans l'oxyde d'uranium. On fournit des données statistiques pour montrer la précision et l'exactitude des méthodes.

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SPEKTROPHOTOMETRISCHE BESTIMMUNG VON WOLFRAM IN MOLYBDÄN

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Zusammenfassung—Ein Verfahren zur spektrophotometrischen Bestimmung von Wolframspuren in Molybdän wird beschrieben. Die Trennung beruht auf dem verschiedenen Verhalten beider Elemente gegenüber Reduktionsmittel. Zuerst wird das Molybdän mit Thioglykolsäure reduziert und als Molybdän(V)-thiocyanatokomplex extrahiert. Nach Reduktion mit Titan(III)-chlorid wird Wolfram als Wolfram(V)-thiocyanatokomplex extrahiert und spektrophotometrisch bestimmt. 0,5 μg Wolfram können in 0,1–0,5 g Molybdän erfaßt werden.

DIE BESTIMMUNG kleiner Wolframgehalte in Molybdän ist mit Ausnahme eines spektrophotometrischen Verfahrens,[1] mit dem noch 10 ppm Wolfram erfaßt werden können, bisher nur spektralanalytisch ohne Trennung der beiden Elemente ausgeführt worden. Um das Nachweisvermögen der verschiedenen Bestimmungsmethoden für Wolframspuren voll ausnutzen zu können, ist eine Abtrennung des Wolframs vom Grundmaterial notwendig. Bei dem erwähnten spektrophotometrischen Verfahren erfolgt diese Trennung durch Extraktion des Wolfram(VI) als 8-Hydroxychinolinkomplex, während das mit Hydrazinhydrochlorid reduzierte Molybdän als nichtextrahierbarer Molybdän(V)-Äthylendiamintetraessigsäurekomplex in der wäßrigen Phase zurückbleibt.

Aus der Literatur ist die Extrahierbarkeit der Molybdän(V)- bzw. Wolfram(V)-thiocyanatokomplexe bekannt. So wurde Molybdän nach Reduktion mit Thioglykolsäure[2,3] und Wolfram nach Reduktion mit Zinn(II)-chlorid[4] extrahiert. Außerdem ist ein Verfahren zur Abtrennung von Molybdänspuren von einer Makromenge Wolfram aus thiocyanathaltiger Lösung bekannt.[5]

Es sollte deshalb untersucht werden, ob die Extraktion aus thiocyanathaltiger Lösung auch für die Abtrennung von Wolframspuren aus einer Makromenge Molybdän anwendbar ist. Da Molybdationen leichter als Wolframationen reduziert werden, ist es notwendig, zunächst das Molybdän aus der Lösung zu entfernen, wobei Wolfram aber möglichst vollständig in der wäßrigen Phase verbleiben muß. Anschließend kann dann Wolfram extrahiert und photometrisch bestimmt werden.

MOLYBDÄN-WOLFRAM-TRENNUNG

Abbildung 1 zeigt das Verteilungsverhalten des Molybdän(V)-thiocyanatokomplexes in Abhängigkeit von der Säurekonzentration. Die Probelösung, insgesamt 15 ml, enthält 100 mg Molybdän als Natriummolybdat, 2 ml 60%ige Citronensäurelösung, 2 ml 5 m Ammoniumthiocyanatlösung, 10 Tropfen Thioglykolsäure und der angegebenen Konzentration entsprechende Mengen an Schwefel- bzw. Salzsäure. Nach Zugabe der Thioglykolsäure muß bis zur Extraktion, die mit 15 ml Butylacetat erfolgt, 15 min gewartet werden, damit sich die Reduktion des Molybdän(VI) zu Molybdän(V) vervollständigen kann. Extrahiert man vor Ablauf dieser Zeit, so erhält man kleinere und schwankende Verteilungsverhältnisse.

Zur Ermittlung der Verteilungsverhältnisse wurde der Molybdängehalt der wäßrigen Phase nach Zerstörung der organischen Substanzen durch Abrauchen mit konzentrierter Schwefelsäure spektrophotometrisch mit Phenylhydrazin bestimmt.[6]

Abbildung 2 zeigt die unter gleichen Bedingungen ermittelten Verteilungsverhältnisse für jeweils 200 μg Wolfram in Gegenwart von 100 mg Molybdän. Sie wurden durch Messung der Wolfram-187-Aktivitäten in beiden Phasen erhalten. Die Zugabe

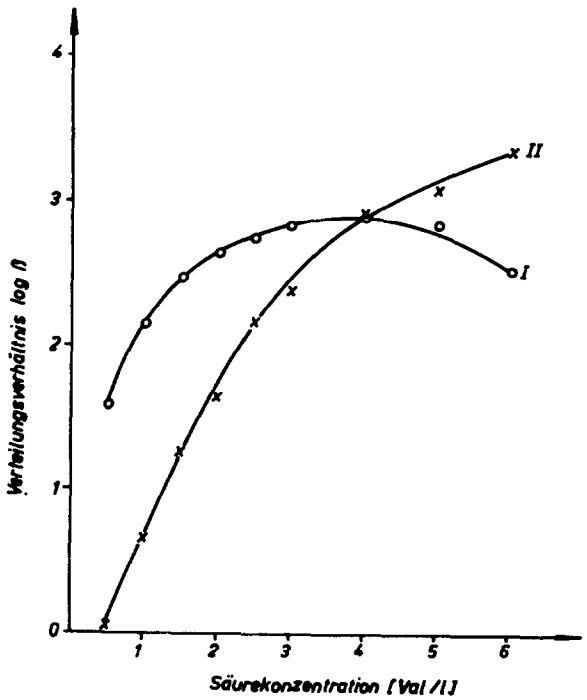

ABB. 1.—Verteilungsverhalten des Molybdän(V)-thiocyanatokomplexes in Abhängigkeit von der Salzsäure- bzw. Schwefelsäurekonzentration bei Extraktion mit Butylacetat.
I—Salzsäure;
II—Schwefelsäure.

der Citronensäure verhindert infolge Bildung nichtextrahierbarer Citratkomplexe die Extraktion des Wolfram(VI).[7]

Zur Ermittlung der für die Trennung optimalen Extraktionsbedingungen sind in Tab. I die Verteilungsverhältnisse für Molybdän und Wolfram und die daraus erhaltenen Trennfaktoren in salz- bzw. schwefelsauren Lösungen zusammengestellt. Unter Berücksichtigung dieser Werte wurde in der Arbeitsvorschrift die Extraktion aus 4 n schwefelsaurer Lösung festgelegt. Diese Bedingungen entsprechen nicht der Regel, nach der optimale Trennwirkung dann erzielt wird, wenn das Produkt der Verteilungskoeffizienten der zu trennenden Elemente 1 ist.[8] Durch die Steigerung der Schwefelsäurekonzentration von 2,5 auf 4 n erhält man aber eine bessere Molybdänabreicherung, so daß schon zwei Extraktionen zur vollständigen Abtrennung ausreichen. Der dabei auftretende Wolframverlust von etwa 5% wird bei der Eichung berücksichtigt.

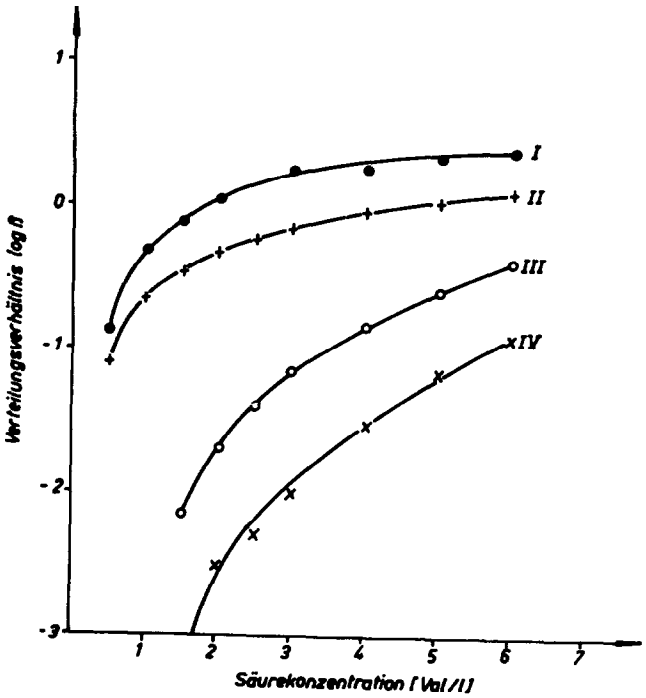

ABB. 2.—Verteilungsverhalten des Wolfram(VI)-thiocyanatokomplexes in Abhängigkeit von der Salzsäure- bzw. Schwefelsäurekonzentration bei Extraktion mit Butylacetat.
I—Salzsäure;
II—Schwefelsäure;
III—Salzsäure in Gegenwart von Citronensäure;
IV—Schwefelsäure in Gegenwart von Citronensäure.

TABELLE I.—VERTEILUNGSVERHÄLTNISSE VON MOLYBDÄN UND WOLFRAM UND TRENNFAKTOREN FÜR DIE MOLYBDÄN-WOLFRAM-TRENNUNG

Säure, n	H_2SO_4			HCl		
	β_{Mo}	β_W	$\frac{\beta_{Mo}}{\beta_W}$	β_{Mo}	β_W	$\frac{\beta_{Mo}}{\beta_W}$
0,5	1,1	0,0001	11000	38	0,0002	190000
1,0	4,5	0,0003	15000	140	0,001	140000
1,5	18	0,0007	26000	290	0,007	41000
2,0	44	0,002	28000	430	0,02	21000
2,5	144	0,005	28000	560	0,04	14000
3,0	248	0,01	28000	690	0,07	9900
4,0	815	0,03	28000	770	0,14	5500
5,0	1220	0,07	18000	690	0,25	2800
6,0	2300	0,14	16000	340	0,40	850

WOLFRAMBESTIMMUNG

Nach Entfernung des Molybdäns befindet sich das Wolfram gemeinsam mit den unter diesen Bedingungen nicht extrahierbaren Verunreinigungen in der wäßrigen Phase. Zur extraktionsphotometrischen Bestimmung wird es nach Reduktion mit Titan(III)-chlorid als Wolfram(V)-thiocyanatokomplex extrahiert. Abbildung 3, die das Verteilungsverhalten des Wolfram(V)-thiocyanatokomplexes in Abhängigkeit von

der Schwefelsäure- und Ammoniumthiocyanatkonzentration zeigt, ist zu entnehmen, daß die Extrahierbarkeit des Wolframs mit steigender Säure- und Thiocyanatkonzentration zunimmt.

Zweckmäßigerweise extrahiert man aber bei einer nicht zu hohen Thiocyanationenkonzentration, weil die Thiocyanwasserstoffsäure, die ebenfalls gut extrahiert wird, sich in der organischen Phase oberhalb einer bestimmten Konzentration unter Bildung der gelbgrünen Isoperthiocyansäure zersetzt, die die photometrische Be-

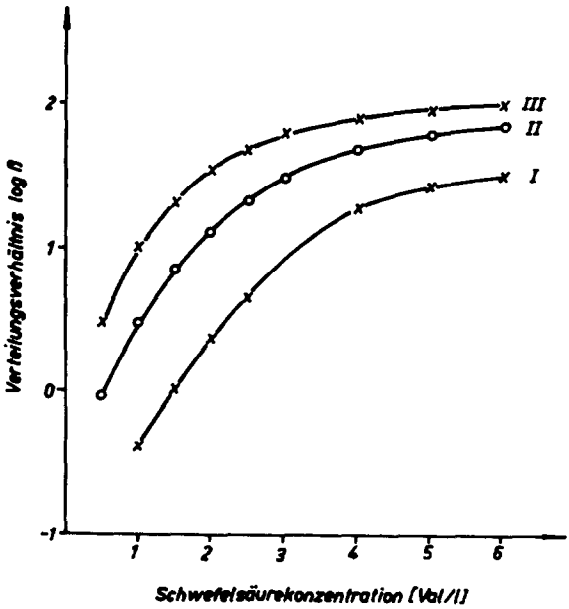

ABB. 3.—Verteilungsverhalten des Wolfram(V)-thiocyanatokomplexes in Abhängigkeit von der Schwefelsäure- und der Ammoniumthiocyanatkonzentration bei Extraktion mit Butylacetat.
I—0,33 m Ammoniumthiocyanat;
II—0,66 m Ammoniumthiocyanat;
III—1,0 m Ammoniumthiocyanat.

stimmung stört. Als ausreichend hat sich die Extraktion aus 0,66 n Ammoniumthiocyanatlösung erwiesen, wobei 97–98% des Wolframs erfaßt werden. Es zeigte sich jedoch, daß bei dieser Konzentration schon Isoperthiocyansäure gebildet wird, die sich aber zusammen mit der Thiocyanwasserstoffsäure ohne nennenswerte Wolframverluste aus der organischen Phase mit verdünnter Salzsäure auswaschen läßt. Tabelle II zeigt das Verteilungsverhalten des Wolfram(V) thiocyanatokomplexes zwischen Butylacetat und Salzsäure verschiedener Konzentration.

Untersuchungen über den Einfluß von Molybdän auf die Wolframbestimmung ergaben, daß die bei einem Trennfaktor von etwa $5 \cdot 10^5$ in der wäßrigen Phase verbleibenden Matrixspuren die Wolframbestimmung nicht stören.

Die Extinktionskurve des in Butylacetat extrahierten Wolfram(V)-thiocyanatokomplexes entspricht in ihrem Verlauf der Kurve der wäßrigen Komplexlösung.[9] Das Extinktionsmaximum liegt bei 400 mμ, der molare Extinktionskoeffizient beträgt dort $1{,}7 \cdot 10^4$.

TABELLE II.—VERTEILUNGSVERHALTEN DES WOLFRAM(V)-THIOCYANATO-KOMPLEXES ZWISCHEN BUTYLACETAT UND SALZSÄURE

Salzsäure, *n*	Verteilungsverhältnis	Reextrahiert, %
1	560	0,18
2	460	0,22
3	340	0,31
4	230	0,43
5	180	0,55
6	150	0,66

ARBEITSVORSCHRIFT

(a) Wolframgehalte von 50 bis 200 ppm

In einem Gemisch von 2 ml Wasser, 2 ml konzentrierter Flußsäure und 1,5 ml konzentrierter Salpetersäure werden 100 mg Molybdän gelöst. Die Lösung wird zur Trockne eingedampft und der Rückstand in 1 ml 8 n Natronlauge aufgenommen. Man neutralisiert die Probelösung und überführt sie mit wenig Wasser in einen Schütteltrichter. Zu dieser Lösung, die etwa 5 ml betragen soll, werden 2 ml 60% ige Citronensäurelösung, 2 ml 5 m Ammoniumthiocyanatlösung, 6 ml 10 n Schwefelsäure und 10 Tropfen Thioglykolsäure gegeben. Nach einer Wartezeit von 15 min schüttelt man 90 sec mit 15 ml Butylacetat. Auf eine vollständige Trennung der Phasen ist zu achten. Die wäßrige Phase wird in einen zweiten Schütteltrichter überführt und die organische Phase verworfen.

Anschließend wird die wäßrige Phase mit 1 ml 5 m Ammoniumthiocyanatlösung und 2 Tropfen Thioglykolsäure versetzt. Nach 5 min schüttelt man 60 sec mit 10 ml Butylacetat und überführt die wäßrige Phase zur Wolframextraktion in einen weiteren Schütteltrichter.

Zu dieser Lösung gibt man 2 ml 5 m Ammoniumthiocyanatlösung, 2 ml 10 n Schwefelsäure und 3 ml 0,1 m Titan(III)-chloridlösung in 4 n Schwefelsäure. Nach 15 min extrahiert man mit genau 10 ml Butylacetat. Danach wird die organische, wolframhaltige Phase dreimal mit 10 ml 1 n Salzsäure 60 sec gewaschen und anschließend zentrifugiert. Die Extinktion der Lösung wird in einer 3-cm Küvette bei 400 mμ gemessen.

(b) Wolframgehalte von 1 bis 50 ppm

Zu der 0,5 g Molybdän enthaltenden Probelösung (7 ml) werden 6 ml 60%iger Citronensäurelösung, 10 ml 5 m Ammoniumthiocyanatlösung, 6 ml 20 n Schwefelsäure und 1 ml Thioglykolsäure gegeben. Nach einer Wartezeit von 15 min wird der Molybdän(V)-thiocyanatokomplex zunächst mit 30 ml Butylacetat und anschließend mit 15 ml Butylacetat 90 sec extrahiert. Die Extraktion des restlichen Molybdäns erfolgt nach Zugabe von 2 ml 5 m Ammoniumthiocyanatlösung und 6 Tropfen Thioglykolsäure mit 15 ml Butylacetat.

Zur wäßrigen Phase gibt man 4 ml 5 m Ammoniumthiocyanatlösung, 2 ml 20 n Schwefelsäure und 3 ml 0,1 m Titan(III)-chloridlösung in 4 n Schwefelsäure. Die weitere Ausführung der Analyse erfolgt wie unter (*a*) beschrieben.

BEWERTUNG DES VERFAHRENS

In Tab. III sind die spektrophotometrisch bestimmten Wolframgehalte einiger Molybdänproben den Resultaten aktivierungsanalytischer Vergleichsanalysen gegenübergestellt.

TABELLE III.—ERGEBNISSE VON WOLFRAMBESTIMMUNGEN IN MOLYBDÄN

Probe	Spektrophotometrie, *ppm*	Aktivierungsanalyse, *ppm*
1	35	33
2	89	92
2	189	205

Zur Ermittlung der Reproduzierbarkeit des Verfahrens wurde der Variationskoeffizient aus Mehrfachbestimmungen verschiedener Analysenproben berechnet. Die erhaltenen Werte mit der Zahl der Freiheitsgrade zeigt Tab. IV. Aus der

TABELLE IV.—REPRODUZIERBARKEIT SPEKTROPHOTOMETRISCHER WOLFRAMBESTIMMUNGEN IN MOLYBDÄN

Probe	Einwaage, *g*	Wolframgehalt, *ppm*	Variationskoeffizient, %	Freiheitsgrade
1	0,1	170	3,8	6
2	0,1	66	5,3	9
3	0,1	18	11,5	6
4	0,5	26	2,7	9
5	0,5	2	20	4

Standardabweichung der Blindwerte ist nach dem 3-σ-Kriterium die Nachweisgrenze des Verfahrens ermittelt worden. Sie beträgt bei einer Einwaage von 0,1 g Molybdän 5 ppm und bei einer Einwaage von 0,5 g Molybdän 1 ppm Wolfram. Die Blindwerte sind in Gegenwart der genannten Molybdänmengen bestimmt worden.

Zur Durchführung von zwei Analysen benötigt man etwa zwei Stunden.

Summary—A procedure is described for the spectrophotometric determination of traces of tungsten in molybdenum. The separation is based on the different behaviour of both elements towards reduction reagents. First the molybdenum is reduced with thioglycollic acid and extracted as molybdenum(V) thiocyanate complex. After reduction with titanium(III) chloride, tungsten is extracted as tungsten(V) thiocyanate complex, which is determined spectrophotometrically. Amounts of 0·5 μg of tungsten can be determined in 0·1–0·5 g of molybdenum.

Résumé—On décrit une technique de dosage spectrophotométrique de traces de tungstène dans le molybdène. La séparation est basée sur le comportement différent des deux éléments vis-à-vis des réactifs de réduction. Le molybdène est d'abord réduit par l'acide thioglycolique et extrait à l'état de complexe thiocyanate-molybdène (V). Après réduction par le chlorure de titane (III), on extrait le tungstène à l'état de complexe thiocyanate-tungstène (V), que l'on dose spectrophotométriquement. On peut doser des quantités de 0,5 μg de tungstène dans 0,1–0,5 g de molybdène.

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SHORT COMMUNICATIONS

Reduction of iridium after oxidation in fuming perchloric acid

(*Received* 23 *December* 1966. *Accepted* 2 *April* 1967)

RECENT papers[1–3] on the electrolytic reduction of iridium in perchloric acid media have contained no reference to the work carried out by Pshenitsyn *et al.*[4] These authors have suggested that the high results obtained in reduction titrations of iridium solutions which have been fumed with perchloric acid are due to reduction products of the acid remaining in combination with the iridium(IV), rather than to the existence of a higher oxidation state of iridium. They attributed the two-stage potentiometric titration curve to the reduction of one of these products followed by titration of the other simultaneously with iridium. McBryde and Cluett[5] also suggested that varying amounts of oxides of chlorine remained in solution in analogous systems. The behaviour of perchlorate solutions of the platinum metals is relevant to our present study of various oxidation states of these metals in which the reduction of iridium has received particular attention.

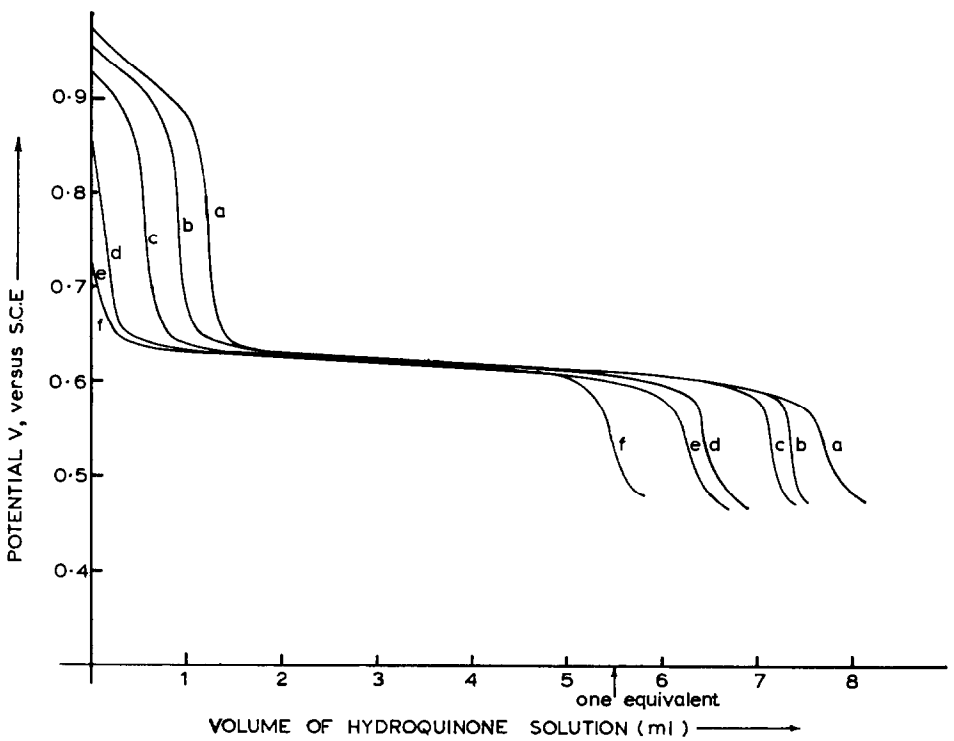

FIG. 1.—Effect of increasing nitrogen flushing time on the reduction titration of iridium after oxidation in fuming perchloric acid.

(*a*) No nitrogen; (*b*) 0·5 hr; (*c*) 1 hr; (*d*) 2 hr; (*e*) 3 hr; (*f*) 8 hr.

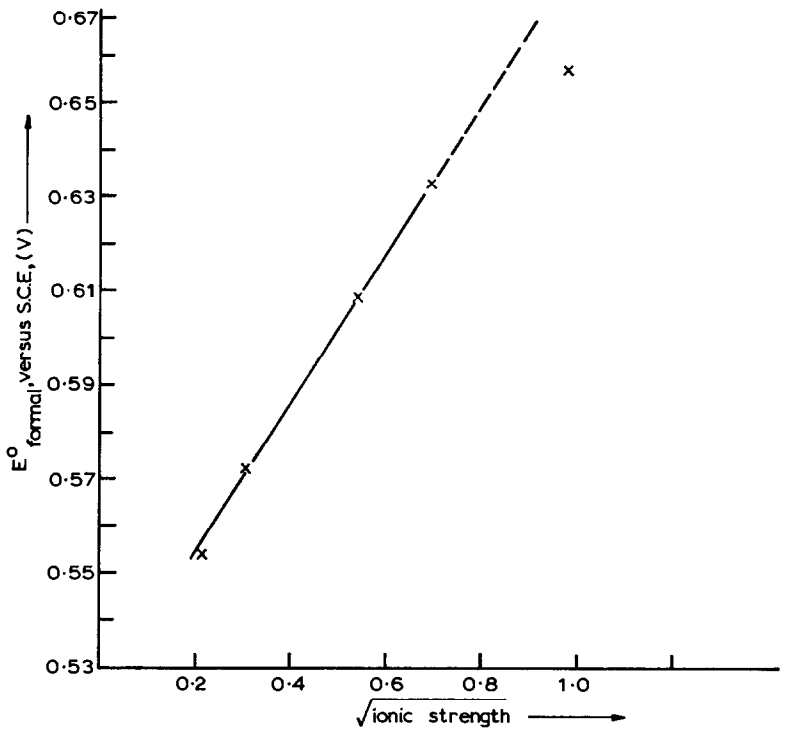

FIG. 2.—Effect of ionic strength on the formal redox potential of the Ir(IV)–Ir(III) system in perchlorate solution.

Despite the inability of Pshenitsyn *et al.* to remove the volatile products by prolonged heating of the solutions, it seemed reasonable to suppose that, if they existed, flushing of the solution with an inert gas for an extended period might accomplish this removal.

EXPERIMENTAL

A stock solution of chloroiridite was prepared from ammonium chloroiridate by reduction with the theoretical quantity of hydrazine hydrochloride. After boiling, the solution was diluted appropriately. The solution was standardised by the gravimetric modification of Pollard's thiourea method[6,7] and was found to contain 1·10 mg of Ir/ml.

Five-ml portions of this solution were evaporated to strong fumes with 1 ml of 60% perchloric acid. After dilution with 10 ml of water each solution was boiled, cooled, diluted to 100 ml, deaerated with nitrogen and titrated potentiometrically with a standard hydroquinone (0·2848 g/l) or iron(II) perchlorate solution. A platinum indicating electrode was used in conjunction with a saturated calomel electrode equipped with a lithium acetate bridge: the cell's potential was measured with a valve voltmeter. Figure 1a is a typical curve and is similar to those obtained by Pshenitsyn *et al.*

Further 5-ml portions of the chloroiridite solution were evaporated to strong fumes with perchloric acid. After dilution, each solution was transferred to a flask and a stream of nitrogen or carbon dioxide was passed through it at a flow rate of 10 l/hr, with the temperature of the solution maintained almost at boiling point. Great care was taken to avoid extraneous reduction and evaporation: an all-glass assembly was used, and the nitrogen was passed through a series of flasks containing acidified permanganate and finally a flask of water before it entered the test solution. After an appropriate time each iridium solution was titrated. Curves b–f in Fig. 1 are those obtained with increasing flushing time. When no gas was admitted the titration curve remained substantially as Fig. 1a even after more than 8 hr.

The two gas streams were equally effective, but use of carbon dioxide generated *in situ*, although showing some reduction in the titration volume, was impracticable since large quantities of carbonates had to be added for a correspondingly small reduction in the volume of titrant needed. In an analogous

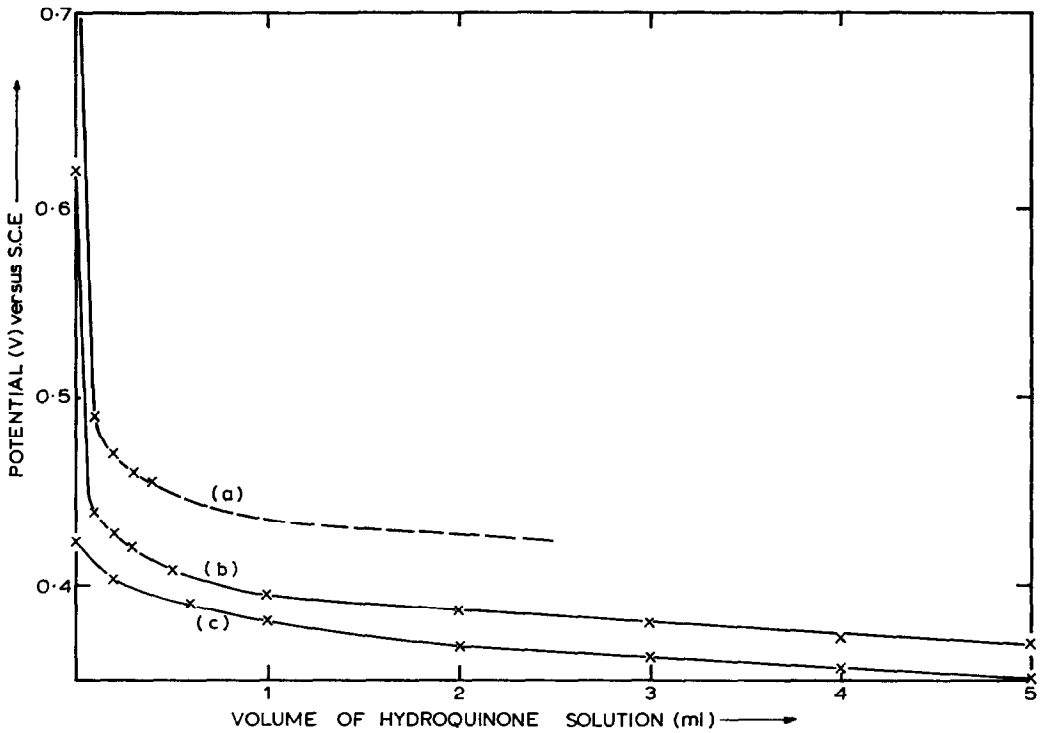

FIG. 3.—Reduction titrations of distillates and fumed perchloric acid.

(*a*) Distillate trap solution;
(*b*) Pure perchloric acid strongly fumed and diluted only;
(*c*) Pure perchloric acid strongly fumed and degassed.

case of chromium oxidized with fuming perchloric acid, *in situ* generation of carbon dioxide proved successful.[8]

RESULTS AND DISCUSSION

A titration, stoichiometric for a one-electron reduction, was obtained after 8 hr or more of nitrogen or carbon dioxide treatment; further extension reduced the volume of titrant needed no further and in all cases the solution at the final inflexion had all the properties of that of iridium(III) alone. No further inflexions could be detected even with large excesses of reducing agent. The titration curve remained very flat compared with that for chloroiridate reduction, which gives a normal curve for a one-electron change, and the slope of a plot of potential *vs.* log [Ir(IV)]/[Ir(III)] gave an apparent electron change of ~4. A further anomaly was found to be the positive shift in the $E^{\circ}_{\text{formal}}$ value with increasing ionic strength of the solution (Fig. 2), similar effects being obtained with perchloric acid and with magnesium perchlorate as added electrolyte. This is the behaviour expected of an anionic system,[9] whereas ion-exchange tests firmly indicated that the iridium is in the cationic form. In view of the findings of Dwyer *et al.*[9] that potentials determined from titration curves of chloroiridate were appreciably lower than those obtained from direct potential measurements of $IrCl_6^{2-}$–$IrCl_6^{3-}$ mixtures, such errors might exist also in the case of the present system, but this should not account for the direction of change of $E^{\circ}_{\text{formal}}$ with ionic strength.

Attempts to collect and identify chemically any volatile products proved unsuccessful even with amounts of iridium up to 50 mg. Since these products would be evolved over the 8-hr period in a volume of some 80 l. of gas their detection would be difficult. However, the distillate-trap solutions had a highly positive potential which decreased on addition of standard hydroquinone solution. Comparison was made with potentiometric titrations of strongly fumed and diluted pure perchloric acid, with and without degassing (Fig. 3) and this suggests the presence of highly oxidizing species both in the strongly fumed perchloric acid and in the distillate-trap solution. No further oxidizing species were detected in the trap after the 8-hr flushing period.

Figure 1 shows that the nitrogen treatment eliminates the first inflexion point relatively rapidly, while the position of the second remains substantially constant. Only when the first inflexion disappears does the position of the second begin slowly to decrease to give ultimately a stoichiometric one-electron reduction titre. This could suggest, if distortion is not excessive, the existence of two distinct oxidizing species, the first of which may be "free" and is removed relatively easily, while the second appears to be more firmly "bound" and is removed with greater difficulty and is characteristic of the presence of iridium in the solution. In general, this work supports the view of Pshenitsyn[4] that strongly-oxidizing volatile species, possibly Cl_2O and Cl_2 originating from the perchloric acid, reach high proportions by some form of association when iridium is present: one of the products gives a separate inflexion in the potential curve, the other is titrated along with the iridium(IV) to give an apparently single step.

This work also indicates that a higher oxidation state of iridium is not likely to be present. Removal of the products by lengthy displacement with an inert gas is similar to what happens in the case of chromium, which is known[8] not to be in a higher oxidation state. Nevertheless, the removal is remarkably slow, which indicates either that the oxidizing products are rather involatile (which should have made them easier to detect in the exhaust gases) or, more likely, that they are at least weakly associated with the iridium or perhaps the perchloric acid in solution. The anomalous shift in the formal electrode potential is receiving further attention in this connection.

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Summary—Evidence is given in support of the theory that high results obtained for reduction titrations of iridium solutions which have been fumed with perchloric acid are due to retention in solution of volatile reduction products of the acid.

Zusammenfassung—Zu hohe Ergebnisse bei Reduktionstitrationen von mit Überchlorsäure abgerauchten Iridiumlösungen könnten vom Verbleiben flüchtiger Reduktionsprodukte der Säure in der Lösung herrühren. Hinweise auf die Richtigkeit dieser Theorie werden angegeben.

Résumé—On donne des arguments à l'appui de la théorie suivant laquelle les résultats élevés obtenus dans les dosages par réduction des solutions d'iridium qui ont été chauffées avec de l'acide perchlorique sont dûs à la rétention en solution de produits de réduction volatils de l'acide.

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Spectrophotometric determination of cobalt with phenanthrenequinone monoxime

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Of the organic reagents employed for the spectrophotometric determination of cobalt[1-8] those with the grouping —CO—C(=NOH)—, present in the monoxime of diketones, give a selective reaction. Nitroso-R-salt continues to be favoured by analysts. Phenanthrenequinone monoxime (PQM),[4-7] a reagent of this class, forms insoluble coloured chelates with a number of metals, particularly cobalt, iron(II), copper and nickel.

The present communication deals with the spectrophotometric study of the reaction of cobalt with PQM and the determination of cobalt. The reagent reacts with cobalt(III) in an aqueous ethanolic medium to give a yellow–orange chelate, extractable into organic solvents, such as benzene, chloroform and carbon tetrachloride. The rate of reaction is slow at room temperature, but can be hastened by heating. The complex is stable towards strong acids.

The reagent compares favourably with Nitroso-R salt in sensitivity and freedom from interferences. Unlike Nitroso-R salt, in solution it is stable to heat and light, and can be stored for long periods without deterioration.

EXPERIMENTAL

Reagents

PQM solution, 0·1% w/v in ethanol. The reagent was synthesized by Goldschmidt's procedure.[8]

Cobalt solution. A stock solution of reagent-grade cobalt(II) sulphate heptahydrate, prepared in doubly distilled water, was standardised gravimetrically as the anthranilate.[9] It contained 2·54 mg of cobalt per ml.

Reagent grade chemicals were used in the study of interferences.

Procedure for spectrophotometric determination

Take a suitable aliquot containing up to 3·0 ppm of cobalt and adjust its pH to 5·0 with 10 ml of acetate buffer. Dilute to 20 ml, and add 2 ml of 0·1% reagent solution.

Allow to stand for at least 1 hr, the minimum time for complete complex formation, or heat on a boiling water-bath for 3 min. Add 20 ml of chloroform and extract the orange complex. Centrifuge the organic phase and measure its absorbance at 470 mμ against a reagent blank, prepared under identical conditions. For larger amounts of cobalt, use larger volumes of chloroform. The absorbance remains constant for at least 48 hr.

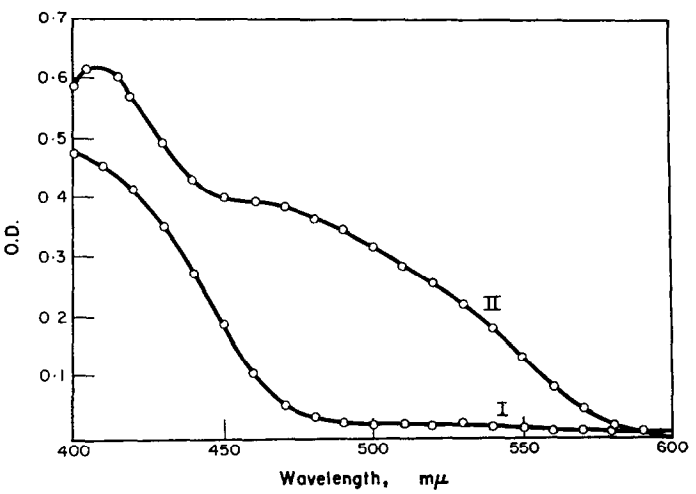

Fig. 1.—Absorption spectra of reagent and its cobalt complex.
I—Reagent *vs.* water; II—Reagent plus cobalt *vs.* reagent.

RESULTS AND DISCUSSION

Spectrophotometric studies

The cobalt complex of PQM has an absorption maximum at 410 mμ and exhibits a broad shoulder between 450 and 470 mμ (Fig. 1). The reagent also absorbs strongly at 410 mμ, but not at 470 mμ, so the latter wavelength has been used for these studies.

A study of solutions in which the mole ratio of cobalt to reagent was varied from 2:1 to 1:10 revealed that a five-fold excess of the reagent is required for full coloration. However, a ten-fold excess was maintained in subsequent studies.

The effect of pH on stability of the complex was determined by preparing a series of solutions varying in pH from 3·72 to 9·0. The absorption maximum (and the wavelength at which it occurs) remain unchanged between pH 4·45 and 8·0. Thus rigid control of pH is not necessary, and sodium acetate-acetic acid buffer of pH 5·0 was employed in the determinations.

Validity of Beer's law and sensitivity of the reaction

The complex was found to obey the Lambert-Beer law over the concentration range 0–3·0 ppm of cobalt at 470 mμ. The optimum range, evaluated by a Ringbom[10] plot, is 0·60–2·4 ppm. The sensitivity of the colour reaction according to Sandell's definition is 0·00336 μg of Co/cm² at 470 mμ for 0·001 absorbance. The molar absorptivity is $17{\cdot}5 \times 10^3$.

Composition and apparent instability constant

For evaluating the composition of the cobalt-PQM complex, equimolar solutions ($1 \times 10^{-4}M$) of cobalt and reagent were employed. Job's method of continuous variations,[11] extended to a two-phase system by Irving and Pierce[12] (Fig. 2) and the mole-ratio method[13] (Fig. 3) indicate the formation of a complex of definite composition between cobalt and the reagent in the mole ratio of 1:3. This was further confirmed by analysis of the extracted chelate and is in conformity with the composition reported previously.[5–7] The 1:3 complex seems to contain tervalent cobalt as do the cobalt chelates with nitroso-naphthols.[14]

The apparent instability constant K, calculated from the equation

$$K = \frac{(\alpha C)(n\alpha C)^n}{C(1-\alpha)}$$

is $2{\cdot}34 \times 10^{-15}$ (where C is the concentration of the complex in mole l^{-1} and n is 3).

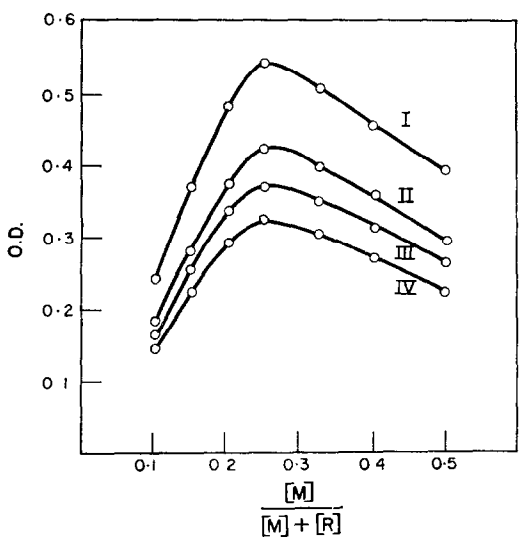

FIG. 2.—Composition of cobalt–PQM complex by Job's method, at pH 5·0. Total molarity: $1 \times 10^{-4}M$. I—400 mμ; II—440 mμ; III—470 mμ; (IV)—500 mμ.

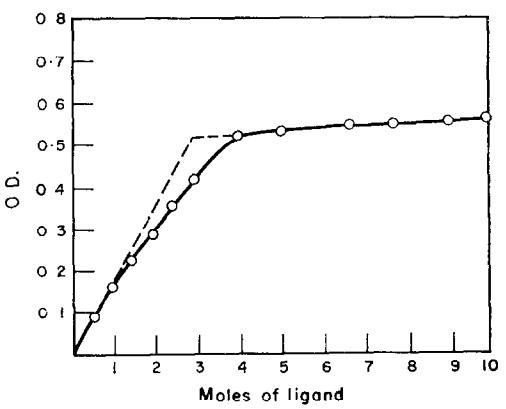

FIG. 3.—Mole-ratio method pH 5·0, 470 mμ; concentration of cobalt = $3 \times 10^{-5}M$

The degree of dissociation α is calculated from the relationship[15]

$$\alpha = \frac{E_m - E_s}{E_m}$$

where E_s is the absorbance at the mole ratio 1:3 and E_m is the absorbance that would have been observed at the point in the absence of dissociation. The E_m and E_s values are 0·55 and 0·42 at a cobalt concentration of $3 \times 10^{-5}M$ and α is thus 0·236.

Effect of diverse ions

Synthetic solutions, containing known quantities of cobalt and varying amounts of diverse ions were prepared and the cobalt was determined. Calcium, barium, strontium, magnesium, vanadium, aluminium, beryllium, bismuth, chloride, tartrate, citrate, nitrate, sulphate, iodate, sulphite, thiocyanate, malonate, phthalate, chlorate, perchlorate and chromate ions do not interfere with the determination even when present in a thousand times the cobalt concentration. EDTA and NTA interfere even in traces.

Copper, nickel, iron, mercury, silver and palladium also form extractable complexes with the reagent. Arsenic, antimony, platinum, gold and tin, though themselves not extracted, affect the recovery of cobalt.

Palladium is removed by precipitating it from highly acidic solutions (0·1*M* hydrochloric acid) with PQM as reagent,[16] centrifuging and analysing the supernatant layer for cobalt or by precipitating the palladium at pH 1·00 and extracting it into chloroform. Iron(II) forms a green complex. Interference from it is eliminated by oxidation with hydrogen peroxide in the presence of sodium citrate in the cold. Silver and mercury are removed by precipitation as chloride and iodide respectively. It is possible to extract cobalt in the presence of copper by adding excess of iodide or thiosulphate. The iodine liberated must be reduced with sodium sulphite. Thiourea can also be used to mask copper. Nickel–cobalt mixtures can be dealt with by precipitating both metals and adding

TABLE 1.—EFFECT OF FOREIGN IONS ON THE DETERMINATION OF 1·2 ppm OF COBALT

Ion	Concentration tolerated, *ppm*
Silver	162
Gold	60
Platinum	150
Nickel	30
Copper	130*
	95†
	500‡
Lead	400
Palladium	500
Cadmium	550
Iron	420§
Manganese(II)	250
Uranium(VI)	5000
Molybdenum(VI)	4000
Arsenic(III)	375
Antimony(III)	1000¶
Selenium	750
Tellurium	1250
Mercury(II)	2000†‡
Oxalate	500
Thiosulphate	550
Phosphate	700
Ammonium	1500

Interferences are removed by addition of:
* Sodium thiosulphate § Sodium citrate and hydrogen peroxide
† Potassium iodide ¶ Tartaric acid.
‡ Thiourea

4*M* hydrochloric acid which decomposes the nickel complex, leaving the cobalt complex unaffected. Results are given in Table I.

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Summary—Phenanthrenequinone monoxime reacts with cobalt to form a yellow–orange insoluble 1:3 (cobalt:ligand) complex which is extractable into chloroform in the pH range 4·45–8·0. The determination of cobalt is carried out at 470 mμ. Beer's law is obeyed over the concentration range 0–3·0 ppm of cobalt. The sensitivity is 0·00336 μg of Co/cm^2 for 0·001 absorbance. The effect of a number of foreign ions has been studied.

Zusammenfassung—Phenanthrenchinonmonoxim reagiert mit Kobalt zu einem gelborangen unlöslichen 1:3-(Kobalt:Ligand)-Komplex, der sich bei pH 4,45–8,0 in Chloroform extrahieren läßt. Kobalt wird bei 470 nm bestimmt. Das Beersche Gesetz gilt bei 0–3,0 ppm Kobalt. Die Empfindlichkeit beträgt 0,00336 μg Kobalt/cm^2 bei der Extinktion 0,001. Der Einfluß einer Anzahl von Fremdionen wurde untersucht.

Résumé—La monoxime de la phénanthrènequinone réagit avec le cobalt pour former un complexe jaune orangé insoluble 1:3 (cobalt: ligand) qui est extractible en chloroforme entre pH 4,45 et 8,0. Le dosage du cobalt est mené à 470 mμ. La loi de Beer est observée pour les concentrations en cobalt allant de 0 à 3,0 ppm. La sensibilité est de 0,00336 μg de Co/cm^2 pour une absorbance de 0,001. On a étudié les effets d'un certain nombre d'ions étrangers.

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Determination of sorbic acid with sodium chlorite

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THE diene structure of sorbic acid suggests the possibility of its determination by a method similar to that used to measure the degree of unsaturation of fats and fatty acids. Such attempts included those by Maurel and Touyé,[1] who tried to use iodine monobromide (Hanus method) or iodine trichloride (Wijs method) in a way resembling the determination of iodine number in fats, but were not satisfied with the results obtained. Spanyár and Sándor,[2] using a bromate–bromide mixture, obtained a good quantitiative bromination in useful analytical conditions, and proposed a method applicable to complex foods, with a maximum error of ±5%.

Using a similar procedure but another halogenation mixture, we have developed a new method for the determination of aldrin (1,2,3,4,10,10-hexachloro-1,4,4*a*,5,8,8*a*-hexahydro-1,4,5,8-dimethanonaphthalene), the halogen being added to the "reactive" double bond in the unchlorinated ring and the excess being determined iodimetrically or potentiometrically.[3,4]

Starting from these and other results we have tried to use sodium chlorite in hydrochloric acid medium for the determination of sorbic acid (hexa-2,4-dienoic acid).

EXPERIMENTAL

Reagents

Sodium chlorite, 0·1*N*. Dissolve 2·25 g of anhydrous sodium chlorite (*p.a.*) in doubly distilled water and make just alkaline with sodium hydroxide. The solution is stable for several months if kept in the dark and at low temperature (refrigerator). The solution is standardised with 0·1*N* thiosulphate, in sulphuric acid medium in the presence of potassium iodide, starch being used as indicator. The solution can be diluted if required.

Procedure

Take a 5- or 10-ml aliquot, containing 2–25 mg of sorbic acid, in an iodine flask or a well-stoppered conical flask. From a burette add 10 ml of sodium chlorite solution and then rapidly add 6 ml of 8*M* hydrochloric acid from a graduated cylinder. Swirl the flask and close it with a ground-glass stopper.

The solution gradually becomes yellow–green, reaching an apparently constant colour in a few seconds. After 30–90 sec add 5 ml of 10% potassium iodide solution rapidly but carefully down the flask walls. To prevent loss of iodine agitate the closed flask gently until the solution becomes homogeneous. Then mix the solution well, wash down the walls with distilled water and immediately titrate to pale-yellow, add 1–2 ml of starch solution and continue the titration until the solution becomes colourless.

The quantity of sorbic acid in the aliquot titrated is $56{\cdot}1\,f(V_1 - V_2)$ mg where V_1 and V_2 are the volumes of f *N* thiosulphate consumed by a blank and the sample respectively. More dilute thiosulphate (0·01 or 0·05*N*) may be used if desired.

RESULTS AND DISCUSSION

The reaction on which the determination is based appears to be chlorination at the 2 and 5 positions leading to a double bond at the 3,4 position:

$$HClO_2 + 3HCl = 2H_2O + 2Cl_2$$

$$CH_3{-}CH{=}CH{-}CH{=}CH{-}COOH + Cl_2 \rightarrow CH_3{-}CHCl{-}CH{=}CH{-}CHCl{-}COOH$$

A similar reaction forms the basis of the Spanyár and Sándor method,[2] though in the original work its mechanism is not discussed by the authors. Maurel and Touyé,[1] in trying to apply this method to the determination of pure sorbic acid obtained recoveries of about 50%. In contrast, we obtained a good recovery. The explanation of this contradiction most probably lies in the fact that the earlier authors considered that addition took place at both double bonds. Some results for pure sorbic acid solutions are shown in Table I.

TABLE I.—DETERMINATION OF SORBIC ACID

Sorbic acid		Difference, *mg*
Taken, *mg*	Found, *mg*	
2·50	2·47	−0·03
2·50	2·57	+0·07
2·50	2·52	+0·02
5·00	4·94	−0·06
5·00	5·16	+0·16
6·00	6·08	+0·08
7·50	7·39	−0·11
7·50	7·50	nil
10·00	10·28	+0·28
12·50	12·45	−0·05
12·50	12·70	−0·20
15·00	15·03	+0·03
15·00	14·83	−0·17
17·50	17·62	+0·12
17·50	17·48	−0·02
20·00	20·21	+0·21
25.00	25·31	+0·31
25·00	25·00	+0·00

The precision and reproducibility are influenced by the conditions of halogenation. To ensure quantitative addition an excess of reagent is necessary. In the conditions specified, reaction is complete in 30–90 sec. The rate of the reactions is determined by the excess of sodium chlorite added. The end of the reaction is indicated by cessation of the colour change to yellow–green. Prolongation of the reaction beyond this time is neither necessary nor useful, because it allows loss of chlorine. Premature addition of iodide, before the yellow–green colour is obtained, gives low results, and so may too small an excess of chlorite reagent. If a large excess of chlorite is used, the reaction is rapid, the yellow colour appears in 4–6 sec and iodide must be added immediately to prevent loss of chlorine. The speed of addition is greater than that of bromine or iodine.

Interferences

A few substances which are used for food conservation and can exist together with sorbic acid in foods have been tested for possible interference. Benzoic, citric and formic acids do not affect the determination; salicylic acid consumes a small quantity of reagent, and sulphite interferes. The effects of maleic and fumaric acids were not investigated.

TABLE II.—DETERMINATION OF SORBIC ACID IN VEGETABLE PRODUCTS*

Extraction method	Sorbic acid added,† *mg*	Sorbic acid found, *mg*	Difference, *mg*	Recovery, %
Ether extraction	2·50	2·35	−0·15	94
	10·00	9·31	−0·79	93
	15·00	14·01	−0·99	93
	20·00	21·80	+1·80	109
Chloroform extraction	5·00	4·52	−0·48	90
	10·00	9·00	−1·00	94
	15·00	16·30	+1·30	107
Steam-distillation and ether extraction	10·00	8·50	−1·50	85
	15·00	14·00	−1·00	93
	15·00	13·28	−1·72	88

* Tomato juice, wine and fruit pulps.
† Added before extraction.

Determination of sorbic acid in food

The sorbic acid must first be extracted from the food sample with solvents or steam to give a solution of the required concentration. We tried three schemes for extraction. The first was the ether extraction at pH 1–2 used by Spanyár and Sándor,[2] followed by stripping of the sorbic acid with an alkaline aqueous phase. We also tried evaporating the ether extract at room temperature and redissolving the residue in 5 ml of 0·5% sodium hydroxide solution. The same procedure was used with a chloroform extraction[5] but persistent emulsions appeared, especially when alkaline solutions were used.

We also used the Sudario[6] and the Schmidt[7] methods based on steam-distillation of sorbic acid. The principal disadvantage was the need to collect a large quantity of distillate to ensure the quantitative removal of the sorbic acid, and the final solution was too dilute to be used directly and had to be concentrated either by evaporation (after it had been made alkaline) or by extraction.

The results obtained were influenced by the extraction method used and the relative error was never less than 6%. However, the procedure can be successfully used for the determination of sorbic acid in various samples and has the advantage of considerable rapidity.

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Summary—A new method for the determination of sorbic acid is proposed, using sodium chlorite in hydrochloric acid medium as reagent. In these conditions the hydrochloric acid is oxidized to chlorine which adds on to the double bonds of the sorbic acid. The addition is rapid (30–90 sec) and for this reason the determination is more rapid then others similar to it. Sorbic acid has been determined in foods by this method, after a preliminary solvent extraction or steam-distillation.

Zusammenfassung—Eine neue Methode zur Bestimmung von Sorbinsäure mit Natriumchlorit in Salzsäure als Reagens wird vorgeschlagen. Unter diesen Bedingungen wird Salzsäure zu Chlor oxidiert, das sich an die Doppelbindungen der Sorbinsäure addiert. Die Addition geht schnell (30–90 sec); aus diesem Grund geht die Bestimmung schneller als andere, ähnliche Methoden. Auf diese Weise wurde Sorbinsäure in Lebensmitteln nach vorausgehender Extraktion oder Wasserdampfdestillation bestimmt.

Résumé—On propose une nouvelle méthode de dosage de l'acide sorbique, en utilisant comme réactif le chlorite de sodium en milieu acide chlorhydrique. Dans ces conditions, l'acide chlorhydrique est oxydé en chlore qui s'additionne sur les doubles liaisons de l'acide sorbique. L'addition est rapide (30–90 sec) et, pour cette raison, le dosage est plus rapide que les autres qui lui sont similaires. On a dosé l'acide sorbique par cette méthode dans des aliments, après extraction par solvant ou entraînement à la vapeur préliminaires.

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Decomposition of thiosulphate in acidified oxidants

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THE reaction of thiosulphate with iodine is not immeasurably fast, but proceeds *via* the following reactions:[1,2]

$$S_2O_3^{2-} + I_3^- \longrightarrow S_2O_3I^- + 2I^-$$

$$S_2O_3I^- + S_2O_3^{2-} \xrightarrow{\text{slow}} S_4O_6^{2-} + I^-.$$

Experiments have shown that both chloride and nitrite can compete successfully with the iodine in the oxidation, altering the stoichiometry (in the latter case forming a mixture of thiosulphate and sulphate and ultimately regenerating the nitrite).[2] Apparently, no comparable study has been made of the combined effects of acid and oxidant on thiosulphate although extensive literature exists on the acid decomposition of thiosulphate[3,4] as well as on its behaviour with selected oxidants in limited pH ranges.[5] This paper summarizes some of the results of such an investigation.

EXPERIMENTAL

Reagents and solutions

Reagent-grade chemicals and distilled water were used in all of the studies. The oxidants and thiosulphate were prepared and standardized in conventional ways. The acids were standardized against sodium carbonate, Methyl Orange being used as indicator and the end-point being compared with a reference solution.

Procedure

The tetrathionate produced when thiosulphate was added directly to a solution containing a known, but excessive, amount of oxidant and a known amount of strong acid was determined as follows: the unreacted oxidant was reduced by addition of sulphite, excess of sulphite was added, and the pH of the solution was adjusted to 10 (at this pH $S_4O_6^{2-}$ reacts with SO_3^{2-} to regenerate $S_2O_3^{2-}$), formaldehyde was added (to complex any unreacted sulphite) and the regenerated thiosulphate was titrated iodimetrically. This procedure, known as the Wollack titration, has been described previously.[6]

In those cases in which the end-point in the iodimetric finish faded, the pH was carefully adjusted to between 4·5 and 4·8 before the titration was completed. When either chloramine-T or iodate was used as oxidant, the destruction of the unreacted oxidant could not be observed visually; in these experiments 5 ml of 30% sulphite solution, empirically determined to be a slight excess, were added; the procedure described above was then followed.

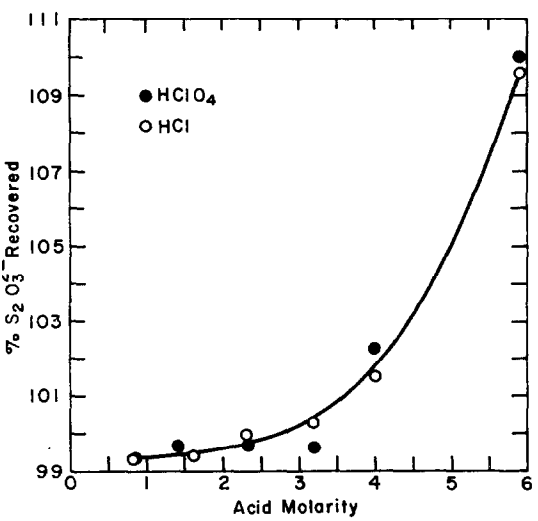


FIG. 1.—The effect of acid on the iodine oxidation of $S_2O_3^{2-}$.

TABLE I.—EFFECT OF TIME OF STANDING OF THE ACIDIFIED THIOSULPHATE IODINE REACTION MIXTURES ON THIOSULPHATE RECOVERIES

Time of standing, *min*	[Acid], *M*	% Thiosulphate found	
		HCl	$HClO_4$
5	2·4	100·0	99·7
	3·2	100·3	100·0
	4·0	101·5	102·3
	5·9	109·6	110·0
60	2·4	100·5	100·0
	3·2	101·3	101·9
	4·0	101·5	102·3
	5·9	118·5	126·3

RESULTS

The results shown in the figures and tables can be summarised as follows.

(*a*) When acidified iodine is used as oxidant, recoveries of thiosulphate increase with increasing acidities (Fig. 1); when no acid is present, low values are obtained because in neutral solution partial oxidation to sulphate occurs. The recoveries from solutions containing $<4{\cdot}0M$ acid remain about the same with increasing time (Table I) which reflects the relatively slow rate at which tetrathionate is decomposed either by iodine[1] or acid.[8] Similar recoveries from perchloric acid and hydrochloric acid media argue that it is the hydrogen ion which affects the reaction and not the anion of the acid. (Conversion of thiosulphate exclusively into tetrathionate would, of course, simply give 100% recovery of thiosulphate. As will be shown later, the high values are believed to arise because the thiosulphate is converted into higher polythionates.)

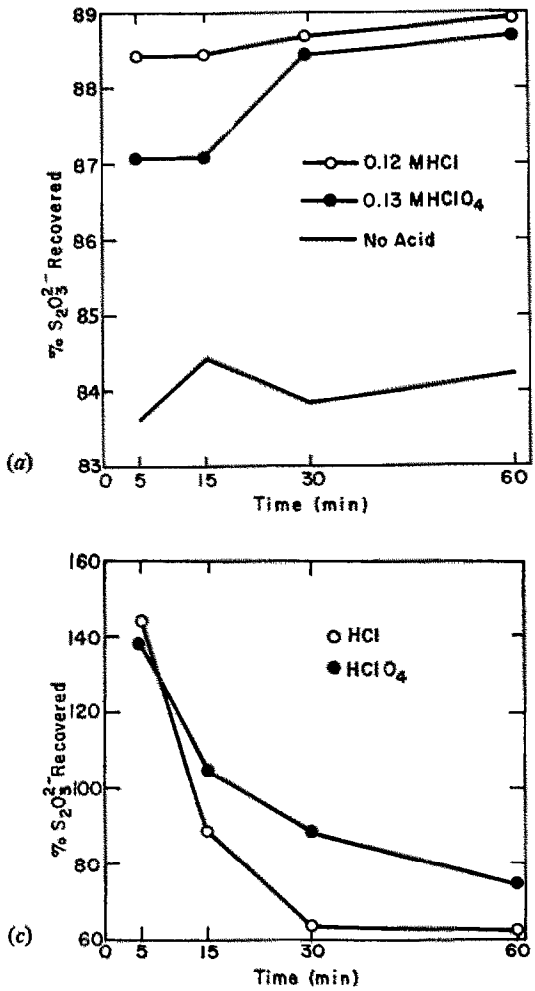
(*b*) When acidified permanganate is the oxidant, thiosulphate recoveries are low (Fig. 2). Increasing the acidity (the range over which this can be done is limited by side-reactions) increases the recovery by about 4%. The recoveries do not vary widely with time. Dithionic acid is known to be a product of acidified permanganate oxidations of thiosulphate; it is reasonably stable towards strong oxidants and would not be expected to react with sulphite. Recoveries of thiosulphate would be expected to be low if dithionic acid were a reaction product; however, consistent recoveries of thiosulphate imply that, under the conditions used, the majority of the thiosulphate is converted into polythionate.

(*c*) The recovery of thiosulphate in acidified iodate solutions depends on the acid used, its concentration and the reaction time (Fig. 2b and Table II). Iodine chloride is, no doubt, an intermediate when oxidation takes place in $6M$ hydrochloric acid. Carrier and Delpla[10] also found that the concentration of hydrochloric acid had a very significant effect on the oxidation; their results indicated that in $<0{\cdot}2M$ hydrochloric acid increasing the acidity increased the amount of sulphate produced, whereas ours suggest that polythionate formation is favoured. The difference may arise because of the large difference in acidities and in experimental procedures, or both suggestions may be true, *i.e.*, both the production of sulphate and of polythionate are functions of increasing acidity.

(*d*) When chloramine-T is used, recoveries of thiosulphate are >100% in weakly acid solution and increase with increasing acid concentration (Table II). In a given acid, the recoveries decrease with time (Fig. 2c). No thiosulphate should have been found if quantitative oxidation to sulphate had taken place as suggested by Murthy.[11]

TABLE II.—THE EFFECT OF ACID AND OXIDANT ON THE RECOVERY OF THIOSULPHATE

Oxidant	% Thiosulphate recovered		
	$10^{-3}M$ H^+	$6M$ HCl	$6M$ $HClO_4$
Iodate	96·3	123·3	50·8
Chloramine-T	104·4	137·2	132·3
Iodine	100·0	109·6	110·0



DISCUSSION

The decomposition of thiosulphate yields a variety of products depending upon the experimental conditions *e.g.*, sulphur dioxide, hydrogen sulphide, and polythionates result from acid decomposition, whereas sulphite, sulphate and dithionates are oxidation products. Because only those compounds containing bivalent sulphur undergo S_N2 reactions with sulphite to regenerate thiosulphate, the Wollack procedure can be used to measure directly the amount of polythionates present in solution.

Quantitative recovery of the thiosulphate would imply reaction to form thiosulphate exclusively. Low thiosulphate values mean that some, if not all, of the reaction products, *e.g.*, sulphate, dithionate, hydrogen sulphide or sulphur dioxide, are not reconvertible into thiosulphate on treatment with sulphite. Acid permanganate and perchloric acid–iodate oxidations illustrate this trend.

Two possibilities exist which would explain the high recoveries of thiosulphate.

1. Tetrathionate produced by normal oxidation of thiosulphate could react as follows:[5]

$$4S_4O_6^{2-} + 6OH^- \longrightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O \qquad (1)$$

The overall stoichiometry for the reaction would then be 5 moles of thiosulphate recovered for every 8 added rather than the 1:2 predicted if the reactions were with sulphite. Reaction (1), however, can only take place in very strong base (pH > 14).[5] Since the highest pH value reached during the entire procedure is when the tetrathionate is reconverted into thiosulphate with sulphite at a pH of 10, and because recoveries from iodine oxidations in weakly acidic media show that at pH 10 the preferential reaction is with sulphite, this cannot be a plausible explanation.

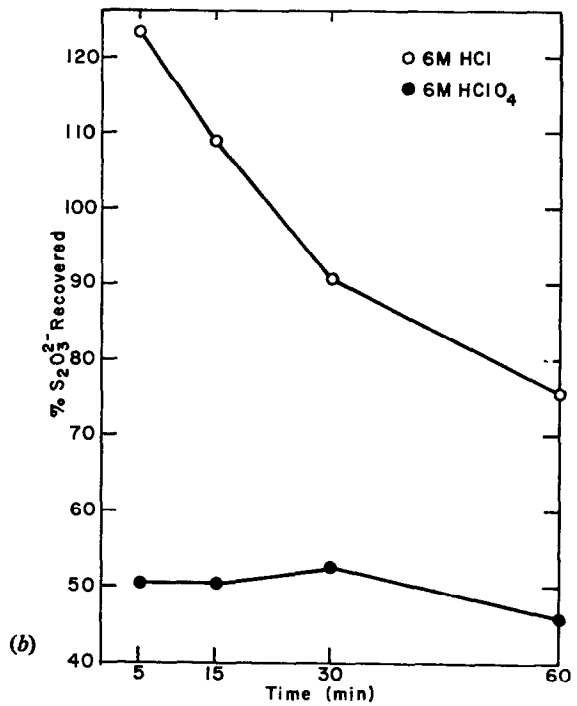


FIG. 2.—The effect of time on the oxidation of $S_2O_3^{2-}$.
(*a*) $KMnO_4$ as oxidant;
(*b*) Iodate as oxidant;
(*c*) Chloramine-T as oxidant.

2. If, however, acid decomposition of the thiosulphate occurs competitively with or to the exclusion of oxidation, polythionates are formed. The polythionates could then react with sulphite in a variety of ways.

$$(1)\quad 3S_2O_3^{2-} + 4H^+ \longrightarrow S_5O_6^{2-} + S(OH)_2 + H_2O$$

$$S_5O_6^{2-} + 2SO_3^{2-} \xrightarrow[pH\ 10]{\text{excess of } SO_3^{2-}} S_3O_6^{2-} + 2S_2O_3^{2-}$$

$$(2)\quad 6H^+ + 5S_2O_3^{2-} \longrightarrow 2S_5O_6^{2-} + 3H_2O$$

$$2S_5O_6^{2-} + 4SO_3^{2-} \xrightarrow[pH\ 10]{\text{excess of } SO_3^{2-}} 2S_3O_6^{2-} + 4S_2O_3^{2-}$$

In the former case the stoichiometry would be 2 moles of thiosulphate recovered for every 3 added while in the latter the ratio would be 5:4; in both cases higher than the 1:2 computed for the Wollack titration itself.

On the basis of these suggestions, the data obtained for all oxidants studied argue that acid decomposition of thiosulphate to produce higher polythionates is occurring competitively with oxidation.

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Summary—The Wollack procedure has been used to study the competition between oxidant and acid for the thiosulphate ion. In concentrated hydrochloric acid solutions of iodine, iodate and chloramine-T, polythionates are the chief products, whereas in acid permanganate substantial amounts of other products occur. Both the concentration of the acid and the acid anion affect the course of the reaction in these solutions. Production of polythionate, an acid-decomposition product, suggests that acid decomposition successfully competes with oxidation.

Zusammenfassung—Das Wollack-Verfahren wurde zur Untersuchung der Konkurrenz zwischen Oxidationsmittel und Säure um das Thiosulfation verwendet. In konzentriert salzsauren Lösungen von Jod, Jodat und Chloramin-T sind Polythionate die Hauptprodukte, wogegen in saurem Permanganat erhabliche Mengen anderer Produkte auftreten. Säurekonzentration und -anion beeinflussen den Reaktionsverlauf in diesen Lösungen. Die Bildung von Polythionat, einem Produkt der Säurezersetzung, deutet darauf hin, daß die saure Zersetzung erfolgreich mit der Oxidation konkurriert.

Résumé—On a utilisé la technique de Wollack pour étudier la concurrence entre l'oxydant et l'acide pour l'ion thiosulfate. Dans des solutions en acide chlorhydrique concentré d'iode, d'iodate et de chloramine-T, les polythionates sont les produits majeurs, tandis qu'en permanganate acide il apparaît des quantités substantielles d'autres produits. Les concentrations tant de l'acide que de l'anion acide affectent la marche de la réaction dans ces solutions. La production de polythionate, un produit de décomposition acide, suggère que la décomposition acide entre avec succès en compétition avec l'oxydation.

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Interfacial free energies of ionic crystals

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THE interfacial free energy between an ionic crystal and its supersaturated aqueous solution is of some importance in classical nucleation theory.[1] In this work, data on the maximum supercoolings attainable with small droplets of aqueous solutions of inorganic salts have been used in conjunction with the Volmer theory of homogeneous nucleation[1] to obtain minimum values of the liquid–crystal interfacial free energy.

The maximum supercoolings observed in droplet experiments by Melia and Moffitt,[2] and Turnbull and Newkirk[3] are shown in Table I. These values are much greater than those previously reported

TABLE I.—CRYSTALLISATION DATA FOR DROPLETS OF AQUEOUS SOLUTIONS OF INORGANIC SALTS (DIAMETER OF DROPLETS APPROXIMATELY 1·0 mm)

Solute	Saturation temperature, °C	S	% Crystallised at 0°C	Reference
NH_4Cl	70	1·5	80	2
NH_4I	35	1·2	100% at 1°C	3
KNO_3	30	3·4	100% at 4°C	2
$KClO_3$	30	3·2	100% at 10°C	2
$K_2Cr_2O_7$	70	12·0	12	2

by other workers[4–7] for bulk samples. This is attributed (*cf.* Vonnegut[8]) to the sequestration of the more active, adventitious, nucleation catalysts which are present in bulk samples as a result of atmospheric (or other) contamination, in a small fraction of the droplets. The remainder may thus be supercooled to a lower temperature. This temperature approaches more closely that temperature associated with true homogeneous nucleation than those reported previously for these solutes.

The Volmer expression[1] for the rate of homogeneous nucleation is

$$\log_{10} J = \log_{10} A - \frac{16\pi\sigma^3 V^2 N}{3(2{\cdot}303RT)^3(\log_{10} S^n)^2} \qquad (1)$$

where J is the nucleation rate, A is the kinetic constant, σ is the interfacial free energy, V is the molar volume of the solid solute, N is the Avogadro number, R is the gas constant, T is the temperature of maximum supercooling in °K, S is the supersaturation ratio $= (m\gamma/m_0\gamma_0)^n$ where m and m_0 and γ and γ_0 represent the molalities and mean ionic activity coefficients of the solute in the supersaturated and saturated solutions respectively at the temperature T, and n is the number of ions produced by one molecule of the solute. Unfortunately, data relating to the molality over the concentration and temperature ranges used in the experiments under consideration are not available. However, data for comparable electrolytes indicate that γ is not strongly dependent on m at the molalities used. Consequently, we shall assume that $\gamma/\gamma_0 = 1$. Assuming also a sensible rate of nucleation $J = 1$ cm^{-3} sec^{-1} and putting $A = 10^{30}$ cm^{-3} sec^{-1}, we calculate from equation (1) the σ_{min} values given in Table II.

TABLE II.—MINIMUM INTERFACIAL FREE ENERGIES OF VARIOUS IONIC CRYSTALS

Solute	σ_{min}, *erg cm*$^{-2}$
NH_4Cl	35
NH_4I	15
KNO_3	57
$KClO_3$	56
$K_2Cr_2O_7$	72

The values of the interfacial free energies obtained in this work are 20 to 30 times those obtained by Chatterji and Singh[9] from their measurements on bulk samples, and approach the values expected[9] for the homogeneous nucleation of ionic crystals from aqueous solution. It follows that the maximum supercoolings observed in the droplet experiments[2,3] closely approach the maximum attainable supercooling of these solutes in aqueous solution.

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Summary—Minimum values of the liquid–crystal interfacial free energy have been obtained from data on the maximum supercooling of small droplets of solutions of ionic crystals.

Zusammenfassung—Untere Grenzwerte der freien Grenzflächenenergie zwischen Flüssigkeit und Kristall wurden erhalten aus der maximalen Unterkühlung kleiner Tröpfchen von Lösungen von Ionenkristallen.

Résumé—On a obtenu des valeurs minimales de l'énergie libre interfaciale liquide-cristal à partir de données sur la surfusion maximale de petites gouttelettes de solutions de cristaux ioniques.

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TALANTA REVIEW*

A CRITICAL REVIEW OF METHODS OF ISOLATING AND SEPARATING THE NOBLE METALS—II†

ION-EXCHANGE AND SOLVENT EXTRACTION

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Summary—This review deals with ion-exchange and solvent extraction methods of separating the seven noble metals, published subsequent to the previous reviews and prior to January 1966. The noble metal species present in solution are discussed in so far as they relate to separation and determination.

THE past decade has witnessed some extension of classical methods of separation as well as new approaches to separational techniques. However, the development in separational methods which in general, constitute the more far-reaching aspects of analytical chemistry, has not been matched by the interest in determinative methods. The recorded determinative methods for the noble metals have been reviewed by the author.[1,2]

One may expect a considerable impetus in separational research from the continually increasing literature dealing with the solution composition of useful analytical systems and from the increasing emphasis on the determination of stability constants and rates of reaction. Given more precise data on the effect of acidity and salt content on the noble metal species existing in solution, the analytical researcher will approach more intelligently the problems of separation by ion-exchange, solvent extraction and chromatography. A case in point concerns an explanation for the failure to separate large amounts of iron from traces of gold by cation-exchange. Although gold in pure solution may not be retained by the resin, the presence of certain base metals produces low gold values. Attempts to solve the problem have indicated changes in the chemical species present in the gold–iron solution. There is also a need for a convincing explanation for the ability of certain cation-exchangers to remove gold from solution; this problem requires more detailed information on the mechanism of adsorption by certain common exchangers. The effect of aging on such methods of separation as ion-exchange or chromatography also needs explanation; some of the more practical instances of this phenomenon have been discussed in previous reviews and examples are also recorded below. Fundamental inorganic researches could provide useful reducing reagents to produce metallic iridium; this reduction is not

* For reprints of this review see advertisement near front of this issue.
† Part I—*Talanta*, 1960, **5**, 1.

accomplished quantitatively by even such theoretically favourable reagents as copper, and precipitation by sulphide is also incomplete. The deleterious effect of fuming with sulphuric acid on the precipitation of rhodium sulphide and on the separation of platinum from the remaining group by oxidation and hydrolysis to hydrated oxides also needs further examination.

Some effort has been made to include in this review the available data dealing with the noble metal species present in solution, particularly in those instances where their character may influence the degree of separation by ion-exchange or chromatography. Unfortunately, this phase of the review is somewhat incomplete. In some instances, especially in the case of Russian literature, the author failed to secure copies of original publications. One may hope that a more complete selection of published literature, with or without translations, will ultimately be made generally available.

The present review deals with literature pertinent to the separation of noble metals and recorded in abstracts from 1 January 1960 to 31 December 1965. An earlier review[3] dealt with publications earlier than this. The separational methods are discussed under the headings ion-exchange, solvent extraction, chromatography, precipitation, and fire assay. It should be noted that some are integral parts of determinative procedures, particularly in the case of solvent extraction integrated with colorimetric techniques. Thus an earlier review[4] included references to solvent extraction methods used before application of colorimetric methods. In such cases the references to restricted solvent extraction are, in general, omitted from the present review. In one or two instances where the author had previously failed to record a spectrophotometric method involving solvent extraction the reference is included here.

An effort was made to avoid repetitive discussion of extractive methods, some of which were developed to apply specifically to spectrophotometric methods for relatively simple systems. More detailed discussions of these will be found in the author's reviews of colorimetric methods. However, emphasis is given here to extraction methods for such restricted mixtures as rhodium and iridium, because of the relative analytical difficulty of their separation, and all extraction methods recorded subsequent to the period covered for the colorimetric review and up to December 1965 are also included.

ION-EXCHANGE

Gold

A new principle was proposed by Kraus *et al.*,[5] who recognized that factors other than ion-exchange play some part in the mechanism of separation by exchangers; in particular they considered the fact that adsorbability of some negatively charged complexes by anion-exchangers was abnormally high, and that a possible explanation involved reactions between the anionic complexes and the organic network. On this basis it was possible that cation-exchangers might adsorb appropriate anions selectively. The cation-exchanger Dowex-50, which contains the same polystyrene–divinylbenzene network as the anion-exchanger Dowex-1, was applied successfully to the isolation of the anion $AuCl_4^-$ or such partially hydrolysed species as $AuCl_3OH^-$ contained in chlorinated solutions of lithium, sodium, potassium and calcium chlorides that were about 0·1*M* in hydrochloric acid. The authors noted the relatively high distribution coefficients for lithium chloride solutions compared with those for hydrochloric acid solutions and the fact that with the anion-exchanger Dowex-1 × 10, while the same divergence occurred in the two media, the coefficients in both cases were of a higher order of magnitude for the salt solution.

This important approach[5] was investigated further by Wang *et al.*[6] who applied the technique to the separation by Dowex-50 × 8 of gold-199 from activated platinum. The authors believed that the mechanism of the anion adsorption by the sulphonated cationites from acid and salt solutions involved basic properties of the oxygen atoms of the neutral sulpho group and that "by the addition of a proton or metal ions, the functional groups of the resins acquire a positive charge." The exchangers used were the cationites Dowex-50 and KU-2, both of which have the functional group

HSO_3^-. Each resin was pretreated with 6–8*M* hydrochloric acid and with chlorine to avoid the reduction of gold. To prepare carrier-free gold-199 from platinum irradiated with thermal neutrons, 1 g of platinum was dissolved in *aqua regia* and the solution was evaporated to 1 ml, diluted with 7–8*M* hydrochloric acid saturated with chlorine, and filtered through 200 mg of Dowex-50 × 8 (200–400 mesh) contained in a 2-mm diameter tube, at a rate of 0·1 ml/min. Platinum was washed from the column with 8*M* hydrochloric acid and gold was eluted with chlorine water; if neutral solutions of gold-199 were required, the platinum was washed out with a hydrochloric acid solution of sodium chloride followed by water to remove the gold. The authors found that the distribution coefficient of gold between resin and solution was directly proportional to the concentration of acid or salt, thus supporting the assumption that the mechanism involved positively charged sulpho groups. The coefficients for salt solutions increased from 9·2 for lithium chloride to 33·5 for caesium chloride. Explanations for these findings were discussed as well as the influence of cross-linkage of the resin on the distribution coefficient.

Beyond question, this technique of separation is worthy of continued examination and it is disappointing that no quantatitive data were provided to indicate the precision and accuracy of the separation, even though the authors did not propose the method as an analytical procedure.

Kraus and Nelson[7] used the tracer ^{198}Au to study the mechanism of adsorption of $AuCl_4^-$ in 0·12–12*M* hydrochloric acid on the basic anion-exchanger Dowex-1. Gold (III) was found to be strongly adsorbed over the whole acid range and the distribution coefficient decreased with increasing acidity.

One of the earliest applications of anion-exchangers to the separation of gold and platinum metals was described by Sussman *et al.*[8] This industrial recovery method involved separation of gold, platinum and palladium as well as chromium, molybdenum, vanadium, *etc.* The recovery of gold, platinum and palladium was more effective by anion-exchange than by adsorption on carbon, and the efficiencies of recovery were Pt > Au > Pd. The authors state that "the method offers interesting possibilities for relatively low cost metal recovery from waste effluents."

A new approach to the separation of gold from large proportions of associated base metals was developed by Ziegler and Matschke.[9] Nitric acid solutions free from hydrochloric acid and containing from 140 to 700 μg of gold with decagram amounts of iron, cobalt, nickel, manganese, copper and lead were adjusted to pH 1–1·5 and passed through filter pulp impregnated with silver sulphide. The pulp or the stained part of it containing the gold (III) sulphide was removed, ignited, treated with *aqua regia*, and evaporated in the presence of hydrochloric acid. The gold was extracted at pH 1–4 with methylene chloride and the absorbance of the organic phase was determined at 394 mμ. This procedure may provide a variety of useful adaptations for the determination of gold in such natural products as ores, concentrates, *etc.* It is noted particularly that 140 μg of gold may be thus separated and determined accurately in solutions containing as much as 284 g of copper or 28 g of iron or lead. One hopes that the recovery will be compared with that attainable by fire assay and the the method can be extended to cover trace amounts of gold.

Anion-exchange resins were used by Darbinyan and Karapetyan[10] to separate gold (3 troy oz/ton) from selenium (0·03 oz/ton) and tellurium (1·3 oz/ton) in ores. Samples were treated with *aqua regia* and then fumed with sulphuric acid. Tin(II) chloride was used to precipitate the three elements, which were then redissolved in *aqua regia*. Gold and selenium were selectively adsorbed from hydrochloric acid at pH 2 by the exchangers ON and AN-F2, and selenium was selectively eluted by 1*M* hydrochloric acid. Gold and tellurium were adsorbed selectively from 6*M* hydrochloric acid by the resins AV-17 and AV-27, and tellurium was eluted by 1*M* hydrochloric acid. The resins were burned and the gold was determined colorimetrically.

Davankov and Laufer[11] collected the chloraurate ion on the chloride form of the resins N–O (59% moisture) and TN (32% moisture). Attempted elution with acids, solutions of thiourea, and dilute solutions of hydrochloric acid in acetone or ethanol were unsuccessful. Gold was recovered by ignition of the resin.

Burstall *et al.*[12] examined the concentration of gold from ores by adsorption of cyanide complexes on anion-exchangers, particularly IRA-400. Gold, copper, nickel, iron, cobalt, zinc and silver were completely adsorbed. Consecutive elutions with 0.2*M* hydrochloric acid, 2*M* sodium cyanide, acetone containing 5% of hydrochloric acid, and 2*M* potassium thiocyanate removed nickel and zinc, copper and iron, silver and gold, and cobalt respectively. By multicycle treatments of effluent and eluate the authors effectively concentrated copper, nickel, iron and gold.

Anion-exchangers were used by Ezerskaya and Markova[13] for the extraction of gold from mill-cyanide, hydrochloric acid, and iodide solutions. The weakly basic resins AN-2F, EDE-10, and Aspatite TM were used batchwise, 200 ml of gold solution being shaken for 1–1·5 hr with a few grams of resin. The amounts of gold ranged from 1·5 g to 15 μg in the case of chloride and cyanide solutions and as little as 1 μg for the iodide solutions. Sulphite was added to the iodide solution to avoid adsorption of iodine by the resin. The copper, zinc and iron complex cyanides were adsorbed with the gold, and the copper interfered with the determination. To avoid this the ignited resin was

selectively extracted with nitric acid. The gold was recovered by ignition and determined polarographically, volumetrically or colorimetrically.

For gold in cyanide solutions, Fridman and Popova[14] used the anion-exchanger AN-2F, 5 g of which adsorbed 23 μg of gold in 30 min; 10 g could adsorb 230 μg from 3 l. of solution. The adsorption of gold was reduced in the presence of iron. Copper and zinc showed relatively little interference.

For the determination of 0·01–100 ppm of gold in copper, Mizuike *et al.*[15] used the chloride form of the anion-exchanger Amberlite IRA-400. After column and batch separations the gold was determined spectrophotometrically and by neutron activation. The results were compared with those obtained by dry assay, solvent extraction–photometric[16] and amalgamation–photometric methods.[17] For the separation by batch process the sample (1–5 g) was dissolved in nitric and hydrochloric acids and diluted to 15 ml per g of copper. Silver chloride was removed and 200 mg of resin were mixed with the solution for 40 min. The resin was filtered off and washed with dilute hydrochloric acid. For the column method the sample was dissolved and diluted to about 12 ml per g of copper. The column, 4 mm in diameter and 20 mm long, contained 0·1 g of dry resin. The dissolved sample was passed through the column at a flow-rate of 1–1·5 ml/min and followed by an acid wash to remove copper. Efforts to elute the adsorbed gold with mixed mineral acids and organic solvents failed and the authors ignited the resin at a temperature below 600° in an alumina crucible. The used of glazed crucibles resulted in low values and wet ashing was incomplete. The ashed residue was dissolved in *aqua regia* and finally the gold was determined spectrophotometrically from an aliquot of the chloride solution.

Alternatively the resin was neutron-activated, and standards were fused as usual, salted with gold, and the gold was gamma-counted. The results for synthetic samples indicated an error of 5–10% over the range 0·4–110 ppm. For crude copper the gold values agreed closely with those obtained by other methods.

Hirano, Mizuike and Iida[18] used the anion-exchanger Amberlite IRA-400, chloride form, to separate gold from copper alloys. The alloy was dissolved in nitric and hydrochloric acids, the solution was passed through the column and the resin was ashed in an alundum crucible. From 0·5 to 100 ppm of gold-198 were determined in the residue with *p*-dimethylaminobenzylidinerhodanine, with an error of 5–10%. Silver was separated as the chloride and palladium was masked by dimethylglyoxime or extracted by ethyl acetate.

For the separation of gold from copper Steele and Hyde[19] used ion-exchange and solvent extraction methods. In the latter case, the solvent was tributyl phosphate mixed with carbon tetrachloride (1 + 2). More than 99·3% of 0·5 g of gold in 20 ml of hydrochloric acid could be extracted by shaking for 1 min if the acidity was >4*M*. Nitric acid depressed the extraction. For ion-exchange Deacidite FF (−50 + 100 mesh) was used in the chloride form. The gold solution was passed through the resin at a rate of 2 ml/min and washed with 2·5% hydrochloric acid. The two separations were of comparable efficiency, and took about a day to complete.

The relative efficiencies of adsorption of tetrachloroaurate(III) anion on cellulose and on the exchanger Dowex-50 were discussed by Beckmann and Lederer.[20] The adsorption coefficient from 6*M* hydrochloric acid was 1·5 for cellulose and 100 for the resin. The authors found that the chromatographic separation was faster than solvent extraction.

Anion-exchange resin was used by Brooks[21] for the determination of gold and other constituents in sea-water. Enrichment factors of up to 2×10^7 were achieved. Columns 0·5 $cm^2 \times 13{\cdot}2$ cm were used to adsorb from 250 l. of sea-water the elements such as gold, thallium and bismuth which had distribution coefficients >38000. The flow-rate was 120 ml/hr applied over about 100 days. After adsorption the column was washed with 2*M* hydrochloric acid and then eluted with 1 l. of 0·25*M* nitric acid. The resin containing the adsorbed gold was ignited and the ash examined spectrochemically at 2676 Å for gold. A single determination indicated a gold content of 0·009 mg/ton of sea water.

Platinum and gold

Sherma and Cline[22] examined the migration of 26 ions on anion-exchange paper with five complexing solvents. The results were reported as a function of the sign of the charge on each ion, determined electrochromatographically. The authors concluded that predicting the results of separations to be attempted by ion-exchange paper chromatography was virtually impossible. In the case of gold and platinum in the tartrate form, on anion-exchange paper SB-2 developed with 0·05*M* tartaric acid at pH 2·2, the anions of both metals showed R_f values of 0. With gold and SB-2 paper in the fluoride form with ammonium fluoride at pH 6·5 as the developing reagent, gold appeared as a cation and platinum as an anion, both with R_f values of 0.

With the paper in the malonate form developed with malonic acid pH 2·2, both gold and platinum appeared as cations with an R_f value of 0. With SB-2 paper in the chloride form developed with diethylenetriamine at pH 11, gold appeared as an anion with an R_f value of 0·20 with streaking back to the origin, and platinum as an anion with an R_f value of 0. With the paper in the chloride form

developed with diethylenetriamine in 0·080*M* hydrochloric acid both gold and platinum appeared as anions with R_f values of 0. In general, these results might encourage development of methods of separation from associated base metals.

For the determination of 0·01–0·4 ppm of platinum in sodium chlorate electrolytic solutions, Iida and Mizuike[23] used Amberlite IRA-400 following reduction of the chlorate and dichromate by heating with hydrochloric acid.

Ruthenium and osmium

In a previous review[3] the present author stated that "no successful application of either cation or anion-exchange separation of osmium and ruthenium has been reported. One would guess that the ease of reduction of osmium salts by organic reagents would preclude such separations. The few reports which include ruthenium *etc.* indicate that reduction or partial hydrolysis or both have prevented quantitative separation." At about that time Hayashi *et al.*[24] used the cation-exchanger IR-120, to separate ruthenium from natural waters. The columns were eluted with 4*M* hydrochloric acid and for mixtures of ruthenium(III) and (IV) the amount of ruthenium bound on the resin was found by using ruthenium-106. The authors state that a considerable amount of ruthenium was adsorbed when the acid concentration of the sample was <0·2*N*.

Contrary to these findings and in part to the present author's predictions, both ruthenium and osmium can be separated by cation-exchange from associated base metals even when <0·1 ppm is present. Zachariasen and Beamish[25] found that when chlororuthenate solution was passed through Dowex-50, at pH 1·5 only 80–90% of the ruthenium was recovered in the effluent. The rest was found on the resin. Treatment of the ruthenium solution with various amounts of sodium chloride increased the recovery, but recovery of ruthenium in the effluent was not quantitative until the ruthenium solution was evaporated to near dryness in the presence of hydrochloric acid and sodium chloride, then diluted with water and adjusted to pH 1·0 before passage through the column. About 25 μg of ruthenium from 5 mg were retained by the column. Application of the method to 20 g of iron-copper-nickel alloys showed negligible losses of ruthenium to the resin. The cause of the losses was discussed by the authors with the guess that low recoveries were associated with aging solutions and presumably caused by the slow production of dissolved cationic species and/or by hydrolysis to hydrated oxides. Spectrophotometric data have been recorded showing a change in solution composition of weakly acidic ruthenium solutions during various aging periods.[26] Zachariasen and Beamish[27] applied their method to the isolation of platinum metals from partially refined concentrates and separated base metals from solutions of the hydrated oxides of palladium, rhodium and iridium.

Several researches have been concerned with the identification of the ruthenium species in aqueous acid and salt solutions. Information of this type can be useful to the analytical chemist who seeks to provide methods of separation, particularly by such techniques as ion-exchange, chromatography, solvent extraction, *etc.* Investigations of ruthenium species present in nitric, perchloric or hydrochloric acids with or without alkali metal salts are of special interest to the analytical chemist. Atwood and De Vries[28] found that in contact with Dowex 50W-×2 polymeric ruthenium(IV) was converted into the monomeric form. In an ion-exchange study of the complexes formed by ruthenium(IV) in hydrochloric and perchloric acids, Paramanova and Latyshev[29] found that micro quantities of ^{106}Ru(IV) in a 1*M* salt solution were hydrolysed after stirring for several days if the acidity was <0·05*M*. The complexes formed in hydrochloric acid <0·07*M* were $Ru(OH)_2^{2+}$, $Ru(OH)_2Cl_2$ (except when 1*M* perchloric acid was present) and $Ru(OH_2)Cl_4^{2-}$. In 0·15*M* and 0·6*M* hydrochloric acid six chloride ions were added to the inner sphere. Presumably $[RuCl_6]^{2-}$ was present. Researches on the species present in aqueous ruthenium(III) solutions have indicated the existence of the cations Ru^{3+} and $RuCl^{2+}$; Connick and Fine[30] have now isolated the *cis* and *trans* isomers of $RuCl_2^+$ and $[Ru(H_2O)_4Cl_2]^+$, which are partially separable by elution from the cation-exchanger Dowex-50.

Van Loon and Beamish[31] applied ion-exchange successfully to the separation of traces of osmium from solutions containing large amounts of base metals. As in the case of ruthenium the separation depends on maintaining osmium in anionic or neutral species over the narrow range of acidity required for the retention of the base metals. Partial hydrolysis of iron, copper and nickel salts in solution was indicated above pH 1·5. Below pH 0·8 incomplete retention of the base metals occurred. The difficulties with ruthenium that were caused by partial hydrolysis were absent in the case of osmium. On aging, osmium solutions at pH 1–11 and in the presence of sodium chloride showed no significant variation in absorption maxima in the range 200–700 mμ. The recommended procedure applied to base-metal alloys involved, as it did in the case of ruthenium, dissolution with hydrochloric acid and small amounts of nitric acid. The large volume of eluate from the cation-exchange separation required evaporation to a volume appropriate for distillation. Small losses of osmium during this evaporation were caused by the presence of small amounts of the three base metals in the first effluent, particularly of copper, and these were avoided by having sulphur dioxide present during the evaporation.[32]

Rhodium and iridium

Karttunen and Evans[33] have applied ion-exchange methods for the isolation of rhodium from solutions of uranium-based fissium alloys. In addition to uranium these solutions contained metals with atomic numbers 40–46. Before passage through the Dowex-50W-$\times$8 exchanger the alloy was dissolved in *aqua regia* containing hydrofluoric acid, and a suitable aliquot of the solution was fumed with perchloric acid to remove fluoride, chloride and ruthenium. Nitric acid was then added followed by tributyl phsophate in carbon tetrachloride to remove uranium. The aqueous phase was then fumed with perchloric acid to remove the remaining traces of chloride, fluoride, ruthenium and nitrate. This fuming process was critical and the permitted volume of 0·5–0·7 ml was cooled and adjusted to within these limits with perchloric acid. The solution was transferred to the resin column which was drained and washed at the rate of 3 ml/min. Palladium was removed with 0·3*M* hydrochloric acid, and then rhodium with 6*M* acid. The rhodium eluate was treated with nitric, perchloric and sulphuric acids to remove organic matter. After fuming, the sulphate solution was treated to yield rhodium chloride which was determined by measuring the absorbance at 475 mμ of its tin(II) chloride complex. Presumably, rhodium in a sulphuric acid solution that has been fumed interferes with the cation-exchange separation.

In a later paper Evans *et al.*[34] recorded an anion-exchange method of isolating rhodium from solutions of plutonium-uranium-fissium alloys. This method, preferred to the earlier procedure which was sensitive to the acidity of the feed solution, required prior separation of uranium as well as multiple fumings of the treated rhodium eluate. The sample was dissolved in hydrochloric and perchloric acids in a sealed tube, and then adjusted to be 8*M* in hydrochloric acid. A suitable aliquot was adjusted in acidity to 8*M*, heated in the presence of nitric acid, allowed to stand for 2½ hr, and passed through Bio-Rad anion-exchanger AG 1 $\times$ 10, 200–400 mesh, at the rate of 35 $\pm$ 5 drops/min with gentle suction applied, and then washed with 8*M* hydrochloric acid. Plutonium was eluted with 0·30*M* hydrochloric acid. The rhodium eluate was first treated to remove organic matter, ruthenium and nitrate by a series of fumings with sulphuric acid, followed by a series of perchloric and sulphuric acid fumings. Rhodium sulphate was converted into the chloride and the absorbance of the tin(II) chloride complex was measured at 470 mμ. The method allowed an efficient adsorption of plutonium, uranium and molybdenum. Plutonium(III), which was not adsorbed, was oxidized by nitric acid to the required oxidation states. The unavoidable leakage of palladium, less than 12 μg, could be tolerated by the tin(II) chloride method.

In several publications the present author has emphasized the varied influence of methods of dissolution of noble metals on methods of separation, or determination, and on the character of interference by associated base metals. Fortunately, precise data are now being recorded for many of the common dissolution reactions of the noble metals. In this connection, there is analytical significance in the report by Kristjanson and Lederer[35] who have described the solution chemistry of rhodium. Unfortunately, the authors confined their study to 6*M* hydrochloric acid solutions on the basis that "this seemed the only concentration for HCl in which analytical ion-exchange separations would be possible." On the contrary, many separations of rhodium have been effected by cation-exchange at pH ~1, *etc.*, conditions under which the identities of the constituents can at present only be guessed. The authors found that dissolution of rhodium hydroxide in 6*M* hydrochloric acid and refluxing at 110° for 1 hr resulted in a 70% conversion into hexachlororhodate(III) and a constituent which formed a strongly adsorbed red-brown band on a Dowex-2 resin column. The same effect was found on dissolving a sample of commercial rhodium chloride in 6*M* acid and aging it for 2 days; with a solution obtained by dissolving in 6*M* hydorchloric acid the residue from evaporation to dryness of rhodium chloride dissolved in 6*M* hydrochloric acid; and with a 6*M* hydrochloric acid solution of rhodium refluxed for 1 hr at 110°. In the case of the dissolution of rhodium hydroxide the evidence obtained by adsorption on the Dowex-2 column and by absorption spectra indicated the following series of reactions with 6*M* hydrochloric acid: cationic and neutral complexes $\rightarrow$ diaquotetrachlororhodate(III) $\rightarrow$ aquopentachlororhodate(III) $\rightarrow$ hexachlororhodate(III). With hexachlororhodate(III) solutions in 6*M* hydrochloric acid there was no detectable shift in absorption maximum on heating, but there was an increase in absorption at the two characteristic maxima. This was interpreted as indicating the presence of a small amount of polynuclear rhodium complexes. In the case of a sample of "ammonium chlororhodite" the change in solution composition on refluxing in 6*M* acid was much the same as with the sodium salt, but the form isolated on the Dowex-2 column suggested the constituent $[Rh(NH_3)Cl_5]^{2-}$.

The authors state that in general refluxing rhodium chloride or hydroxide can accomplish a 95% conversion into the hexachlororhodate. They were thus able to separate rhodium on Dowex-2 from cobalt, copper and ruthenium. It is suggested, however, that any significant amount of the polynuclear complexes would interfere with the separation.

A variety of ion-exchange separations of rhodium from iridium have been proposed. Pshenitsyn *et al.*[36] approached the problem with the guess that complex ions of rhodium and iridium of opposite charges could be obtained through a difference in rates of formation of amine complexes. Although

both rhodium and tervalent iridium reacted with pyridine to form $[M(C_5H_5N)_4Cl_2]Cl$ the former reacted 6·5 times as fast as the latter, the iridium constituent remaining largely as the anion.

Separations by the cation-exchanger KU-2 in the H^+ form were approximately quantitative for rhodium to iridium ratios of 10, 5 and 2 1. With both metals there was a small adsorption of the aquo complexes. In a later paper[37] the authors described a second method of separation which also involved the formation of pyridine complexes. In this case the tervalent indium complex $[Ir(C_5H_5N)_2Cl_4]^-$ was oxidized with chlorine to form the neutral complex $[Ir(C_5H_5N)_2Cl_4]$. Because of the relative insolubility of the latter and the probable adsorption of iridium as a cation the authors preferred to reduce this complex with ascorbic acid back again to $[Ir(C_5H_5N)_2Cl_4]^-$, which was adsorbed quantitatively by the anion-exchanger while rhodium passed through as a cation complex.

The error in iridium determinations was ±3% and for rhodium +4 to −7%. In contrast to the first method, high ratios of iridium to rhodium could be used, ranging from 22 to 98. The amounts of each element were 0·1–10 mg. The order of addition of reagents proved critical. The best results were obtained by chlorine oxidation both before and after the addition of pyridine. Presumably, the authors were not entirely satisfied with the method because further work was being done to find improved conditions for "a more satisfactory separation of rhodium from iridium."

Anion-exchangers have been used to separate rhodium from platinum. Coufalik and Svach[38] applied the method to the determination of rhodium in platinum catalysts. The acid solution of the alloy was treated with sodium hydroxide to precipitate the hydrated rhodium(III) oxide and after a short interval the mixture was adjusted to pH 3·5 with dilute hydrochloric acid. The solution was then passed through anion-exchanger OAL (chloride form) at the rate of 2 ml/min. The rhodium was eluted with 0·2*M* hydrochloric acid and determined colorimetrically with tin(II) chloride. The average recovery was about 96·5% which was acceptable for the required purpose. Platinum was retained on the exchanger and could be eluted only with difficulty by 2*M* ammonia.

Multicomponent metal systems

Polyamidoximes have been used for column or batch adsorption of gold, platinum, palladium, ruthenium and rhodium along with copper, nickel, cobalt, chromium, plutonium, uranium, *etc.*[39] Copper, nickel, cobalt and chromium were complexed at pH 3·4–4·0 while the remaining metals required a pH of 1·0. The amidoximes were made by the reaction of ammonium hydroxide with cyanoethylated cotton, rayon; polyvinyl alcohol fibres containing acrylonitrile, and copolymers of the acrylonitrile with vinyl chloride or vinyl acetate were also used.

For the separation of 0·1–1 mg of rhodium, iridium, platinum and palladium by partition chromatography on ion-exchange resins Moskvin and Preobrazhenskii[40] used a variation of the principle first proposed by Kraus *et al.*[5] and applied by Wang.[6] Sulphostyrene cation-exchange resins KU-2 × 4 and KU-2 × 10 were used. Solutions of the four noble metals with lithium chloride added were evaporated to dryness successively with perchloric acid and water, and several times with hydrochloric acid. Finally the moist residue was treated with hydrochloric acid saturated with chlorine. The precipitate was dissolved in acetylacetone and the solution was added to the exchanger, which was then washed successively with 0·1*M* hydrochloric acid saturated with chlorine, 0·1*M* hydrochloric acid, and acetylacetone saturated with 0·1*M* hydrochloric acid, thus removing the palladium. Then platinum was removed by adding to the resin column a mixture of equal volumes of dibutyl ether saturated with gaseous hydrogen chloride and sulphur dioxide, the latter to reduce the iridium to the tervalent state, and eluting with a 50% solution of n-hexanol or tributyl phosphate in dibutyl ether pretreated with hydrochloric acid and sulphur dioxide. The column was then washed first with carbon tetrachloride and then with the tetrachloride saturated with chlorine to produce iridium(IV) which was then eluted with tributyl phosphate in carbon tetrachloride pretreated with hydrochloric acid and chlorine. Rhodium was then eluted with 4*M* hydrochloric acid. Several procedures for the separation of various combinations of the platinum metals (Rh–Ir, Pd–Rh, Pd–Pt, Ir–Pt) were included in the report, each involving an appropriate selection of eluents.

Blasius *et al.* have extended their earlier contributions dealing with ion-exchange and chromatographic separations of platinum metals. Blasius and Renin[41] approached the problem from the point of view that ion-exchange separations occur not only by a purely electrostatic exchange between anion and anchor groups, but also by a so-called general adsorption at the network including the active groups. On this basis they considered methods which involved precipitation and conversions from anionic to neutral and cationic complexes directly on the exchangers and applied the various conditions which control these reactions in classical systems. Thus with rhodium selective, separation occurred simultaneously with formation of the hydrated oxide. In the case of palladium a pre-wash of a suitable exchanger with a chelating reagent allowed retention on the column and thus a separation from platinum, iridium or rhodium. The exchangers used were Amberlite IRC-50, Permutit RS, Amberlite IR-4B, Permutit ES and Dowex 1. The work was confined to rhodium, iridium, palladium and platinum, in 10–20 mg amounts. The hydroxychloro complexes were prepared in 0·1*M* sodium hydroxide, and nitrite complexes were made by heating with sodium nitrite. Although quantitative

data were not included, the authors stated that quantitative determinations for rhodium, palladium and platinum were made by reduction with hydrazine sulphate in alkaline media and for iridium by precipitation as sulphide. None of these methods is recommended by the present author as particularly accurate.

The authors discussed the effects of the resin groups, cross-linking and dissolution conditions. Difficulties of elution were noted in the cases of the chlorocomplexes and the weakly basic anion-exchanger IR-4B, and with the strongly basic anion-exchangers Permutit ES and Dowex 1. In the case of the oxyhydrate solutions the cation-exchangers Amberlite IRC-50 and Permutit RS allowed the quantitative passage of iridium and platinum. These exchangers in the sodium or ammonium form will retain most of the rhodium and all of the palladium hydrated oxides, both of which can be eluted with 1*M* hydrochloric acid. It is noted, however, that freshly prepared rhodium solution, like iridium and platinum, is not retained by the exchanger. In the case of the nitrito complexes palladium alone is retained by the ammonium form of the cation-exchanger IRC-50. Rhodium, iridium and platinum pass through the exchanger as neutral complexes.

The authors recorded procedures for a variety of separations of groups of two and three metals, but their general applicability was reduced by some incomplete separations though they do suggest new approaches to some separations.

The two-component separations were: palladium from iridium as chlorocomplexes by IR-4B, with elution of iridium by 1*M* sodium hydroxide and palladium by diacetyldioxime and ammonia solution; platinum from iridium, rhodium or palladium as chlorocomplexes by Permutit ES (chloride form) iridium being eluted by 7*M* hydrochloric acid after reduction with iron(II) sulphate, and platinum eluted with the same acid after treatment of the column with sodium sulphite. The iridium eluate contained traces of platinum and the elution of platinum was not complete. Rhodium was separated from platinum by the same method, with some contamination of the rhodium eluate. A procedure was included for the simultaneous separation of rhodium, palladium and iridium from platinum by combination of these methods. Rhodium was separated from palladium or iridium by column precipitation as hydrated rhodium oxide on Amberlite IR-4B. IRC-50, sodium or ammonium form, was also used to separate palladium from rhodium, iridium or platinum by the hydrolytic method. Palladium was first selectively precipitated on the column. In the case of an aged rhodium solution part of the metal was coprecipitated with the palladium. The cation-exchanger IRC-50 was also used to separate palladium selectively from rhodium, iridium or platinum. In this case the chloride complexes were heated with a nitrite solution and palladium alone was bound to the exchanger. On the other hand, these three metals as nitrite complexes were quantitatively adsorbed on the hydroxide form of the anion-exchanger Permutit ES; palladium could then be selectively eluted by ammonia solution, with rhodium or iridium being eluted by 1*M* nitric acid. If platinum were present, it would partly be eluted with palladium. On the other hand, palladium could be selectively isolated from solutions of the four metals by a pretreatment of the cation-exchanger with salicylaldoxime. Palladium was retained as the oxime complex and eluted by 7*M* hydrochloric acid, but traces of palladium were found with each of the other metals.

The authors applied these principles to the separation of rhodium and palladium with either iridium or platinum; and palladium, iridium and platinum. They concluded that the separation of all four elements by using exchangers would be of no advantage compared to classical methods. In the present author's opinion, this situation remains true; for large amounts of metals the wet separations are more accurate and for trace amounts there are chromatographic procedures which provide cleaner separations. However, one may hope that the efforts to improve exchange techniques for the seven noble metals will continue.

A cresolic resin chlorinated to a gain of 20% and then refluxed with *p*-dimethylaminobenzilidene n acetone and concentrated sulphuric acid, isolated, washed and designated as Sel-K_3, was used by Lewandowski and Szczepaniak[42] to separate silver, copper(I), mercury(II), palladium(II), gold(III), platinum(IV) and osmium tetroxide from a solution of some 30 elements including nickel, cobalt, manganese, iron, tin and lead. Osmium tetraoxide was eluted by 1·5*M* hydrochloric acid and the remaining platinum metals by 3*M* hydrochloridic acid. No data were supplied for the noble metals and one may hope that quantitative data will be forthcoming.

Cation-exchange separations of platinum, palladium, rhodium and iridium from assay alloys of iron, copper and nickel have been reported. Dowex 50 × 8 (20–50 mesh) resin was used by Plummer *et al.*[43] to isolate platinum and palladium. The alloy was dissolved in hydrochloric acid, the solution was evaporated to low volume then a little nitric acid was added. After removal of the nitric acid the solution was filtered, and the filtrate was adjusted to pH 1·5, passed through the exchanger, which was then washed with water. The effluent was treated to remove carbon, boron and selenium and then passed through a small column of the same exchange resin. The effluent was practically free from base metals and platinum and palladium could be determined by any convenient method. By a similar procedure Tertipis and Beamish[44] separated iridium from iron–copper–nickel alloys, and Sant and Beamish[45] separated rhodium from these alloys. Sen Gupta and Beamish[46] used the exchange

separation for the recovery and determination of platinum, palladium, rhodium and iridium from the perchloric acid solutions used to eliminate osmium and ruthenium. The Dowex 50W-×8 cation-exchanger has also been used for the separation of platinum and palladium,[47] iridium,[48] and rhodium,[49] from large amounts of copper.

The cation-exchanger KU-2 adsorbs tellurium selectively from 0·01–0·1*M* hydrochloric acid solutions of tellurium, selenium, platinum metals and associated base metals. Solutions of selenium, tellurium, platinum, palladium, copper and nickel were made ammoniacal and passed through the cationite.[50] Selenium and tellurium passed into the filtrate. Copper, nickel and palladium were extracted by cold hydrochloric acid (1 + 1) and platinum by hot acid. At acidities above 0·1*M* part of the tellurium was adsorbed and could be extracted by ammonia. With 0·01–0·1*M* hydrochloric acid and KU-2, tellurium was selectively adsorbed, the platinum metals passing into the filtrate. The accuracy and precision of recoveries of platinum, palladium, rhodium and iridium in amounts of 0·1–5 mg in the presence of 100–200 mg of tellurium were somewhat indifferent. With the ammoniacal solution of platinum and palladium in the presence of copper and nickel the accuracy and precision were of a similar order.

The application of ion-exchangers to the determination of iridium, platinum, palladium and rhodium in solutions from the anodic dissolution of copper-nickel sulphide ores was described by Nadezhina *et al.*[51] These noble metals were quantitatively deposited on the anion-exchanger AV-17 from solutions at pH 2 and containing iron, nickel, cobalt and copper. Only 70% of the ruthenium was deposited although citric acid added to the eluate allowed the adsorption of the remaining ruthenium on a fresh batch of AV-17. This exchanger is similar to Dowex 1 and 2, and Amberlite IR-100. Variations in pH from 2 to 4, and the presence of sulphate, chloride, sodium and potassium were without effect. To determine the platinum metals the resin was burned in the presence of silica and the ash injected into an electric arc run at 12 amp. In an earlier report Nadezhina[52] examined the conditions for rhodium precipitation on two exchange resins. Rhodium was quantitatively adsorbed by EDE-10-p and AV-18 from 1·3*M* hydrochloric acid solutions. These anion-exchangers contain quaternary amino groups and thus have complex forming ability. However, the anion-exchanger AN-2F, which has a complex forming potential but not quaternary amino groups, adsorbed rhodium to a lesser degree. Rhodium was adsorbed most strongly by AV-18 and AV-27. The author also used the anion-exchangers AN-9, AN-1, AV-17 and the cation-exchanger KU-2. At low acidities all of the anion-exchangers adsorb >95% of the rhodium. Under these conditions, the retaining power of the anion-exchangers is equal. It is noted that the author used only rhodium chloride solutions freshly prepared from the metal.

For the separation of platinum metals from associated base metals Anisimov *et al.*[53] used the cation-exchanger KU-2 with 0·3*M* hydrochloric acid solutions. Two g of the resin were used in a column 1·5 cm in diameter and 20 cm long. The results compared favourably with those obtained by the classical hydrolysis in the presence of nitrites.

For the separation and determination of platinum metals in concentrates, Payne[54] integrated classical, ion-exchange and chromatographic methods for use with samples of up to 250 mg of platinum metals. The sample of concentrate was treated in a nickel crucible with hydrofluoric acid to remove silica and then fused with sodium peroxide, and the hydrochloric acid solution of the fused mixture was heated in a distillation flask with sodium chloride and bromate, ruthenium and osmium being collected in a train of receivers containing dilute hydrochloric acid and an end receiver containing ethanolic sodium hydroxide. Osmium was separated from ruthenium by heating the acid receiving solution and collecting in the end receiver. Osmium could then be determined gravimetrically as the hydrated oxide or absorbtiometrically as the thiourea complex. Ruthenium was determined as the metal by evaporation and reduction in hydrogen or spectrophotometically as the thiourea complex.

The pot liquid residue from the distillation was evaporated almost to dryness and the aqueous solution was treated at pH 7 with nitrite to precipitate the base metals selectively. The latter were separated and re-precipitated and, by a system of aliquots, essentially one half of the noble metal content of the pot liquid was treated with hydrochloric acid to remove nitrous fumes and the pH was adjusted to 3 with sodium hydroxide. The remaining base metals were then separated by passage through the cation-exchanger, Zeo-Karb 225. The effluent, containing the nitrited platinum metals, was evaporated in the presence of lithium chloride and fumed in the presence of perchloric acid. The latter was removed by evaporation, hydrochloric acid was added and the solution was evaporated to dryness, this treatment being repeated six to ten times; concentrated hydrochloric acid was added and the volume reduced to 2 ml by evaporation. Solid hydroquinone and hydroquinone dissolved in an isobutyl methyl ketone–hydrochloric acid mixture were added to reduce the iridium, and the organic phase was added to a 35-cm cellulose column prepared from powder slurried with isobutyl methyl ketone and hydrochloric acid. Elution with the reducing solvent was continued with each extract added to the column. Platinum was eluted first, followed by the palladium. The aqueous phases contained the rhodium and iridium. Iridium was selectively extracted by an oxidizing solvent

prepared from hydrochloric acid, sodium chlorate and the acid solvent containing hydrochloric acid and isobutyl methyl ketone. The extract, added to the column, produced a dark-brown band preceding the pink band of rhodium which appeared when the aqueous rhodium phase was subsequently added to the column. The isolated effluents, each containing one of the four metals, were treated by modified conventional methods of determination. The time required for a complete analysis was about one week and the accuracy for mg amounts of metals was about that normally expected from classical methods. Presumably, the methods of separation were not applied to microgram amounts of the metals and with these one might expect high errors from the nitrite separation of base metals contained in the pot liquid. In a footnote the author suggests a modification (addition of tributyl phosphate to the ketone) which decreases the period required for a chromatographic separation. However, platinum and palladium then have similar R_f values.

An ion-exchange separation of gold and noble metals was used by Brooks and Ahrens[55] as a method of concentration prior to spectrochemical determination. In the present author's opinion the course of their investigation would have been modified considerably had the authors been acquainted with the rather extensive analytical literature dealing with their problem. The samples examined were hortonolite dunite, platinum-bearing rock from the Merensky Reef and samples of "Cape granite." Enrichment factors of up to 2000 were obtained from samples of 159–200 g each of which was treated with hydrochloric and hydrofluoric acids, *aqua regia*, sulphuric acid and bromine. Finally a 2*M* hydrochloric acid solution was added to the basic anion-exchanger, Amberlite IR-400, then the eluates obtained first with 0·25*M* nitric acid and then with 1*M* ammonia solution were evaporated to dryness. To remove large excesses of iron the nitrate residue was redissolved in nitric acid and passed thorough a second smaller column; the nitric acid eluate was divided into one fraction containing most of the iron and another containing most of the noble metals. A spectrographic examination was then made of the ignited resin, reagent blank, ammonia fraction and the two acid fractions. No analytical data were provided to indicate the success of the procedure, and to substantiate the authors' prediction of its general applicability.

SOLVENT EXTRACTION

Gold

New and useful extractive methods for gold are being recorded. Trioctylphosphine oxide was used by Holbrook and Rein[66] to produce a gold-bromoaurate complex extractable by chloroform. The recommended range of gold was 20–100 μg. The method was preferred to existing extractions because the absorbance (at 395 mμ) was measured directly on the chloroform extract and there was no appreciable interference from associated base and noble metals. Phosphoric acid was used to complex any iron. Disadvantages are the need for a carefully controlled bromine content in the hydrobromic acid, the fractionating of the chloroform to remove ethanol, and the instability of the gold complex in chloroform solution. It is noted that measurements of the effects of diverse constituents were made without incorporating the dissolution procedure for the gold sample. It should also be recognized that non-interference by individual constitutents added singly provides no assurance of non-interference when they are present simultaneously. Furthermore, the authors' claim for a time advantage over the acetate extraction, considered on the basis of either a few or of many determinations, is invalid. However, the proposed procedure will prove useful as an alternative method or for specific applications. The authors suggested that the method could be used for sulphide ores containing 0·01% of gold but verification for this claim is necessary.

A useful solvent extraction of gold in the presence of very large proportions of platinum, palladium, rhodium, iron, cobalt, nickel and manganese was described by Ziegler.[57] Solutions of the metals containing at least 12% of hydrochloric acid and limited amounts of nitric acid were extracted three times with polyethyleneglycol 400 and the absorbance was measured at 320 mμ. Excellent recoveries were obtained for 60–170 μg of gold. A similar extraction of gold bromide was also described.[58] The method is applicable over the pH range 1–4. The aqueous layer was buffered with disodium hydrogen phosphate and phosphoric acid at pH 0·9–1·4, iron thus being complexed. The gold solution in a little nitric acid was treated with the buffer, potassium bromide was added, then the polyethyleneglycol and 2–3 extractions were made with methylene chloride. Absorbance was measured at 394 mμ. Large proportions of iron, cobalt, nickel, manganese, copper and lead and smaller proportions of bismuth are tolerated. There was interference from palladium and platinum.

In a third application[59] of this approach to the selective extraction of gold the nitric acid solution was treated with sodium saccharinate, phosphate buffer and polyethyleneglycol-400 and extracted three times with the methylene chloride. The absorbance was measured at 315 mμ. There was no interference from large proportions of lead, copper, cobalt, nickel, iron, bismuth and smaller proportions of palladium.

Blyum and Ul'yanova[60] decomposed about one third of an assay ton of ore with *aqua regia*, evaporated to remove nitric acid and dissolved the residue in hydrochloric acid. Tellurium, hydrazine,

filter paper pulp and tin(II) chloride were added to the boiling mixture. The colloidal mass was filtered off, washed and dissolved in *aqua regia*; the liquid was evaporated and then treated with a few drops of hydrochloric acid, a solution of iron(III) chloride and 30% hydrogen peroxide. Finally gold was extracted after addition of a solution of Crystal Violet and toluene, and determined photometrically. Theoretically, procedures such as these ought to produce accurate recoveries of gold in ores but in practice the techniques encourage losses by adsorption and sometimes in the multiple evaporations. In any case, these methods ought to be standardized by procedures which involve an ore of similar composition but free from platinum metals.

Ethyl Violet has also been used in an extractive photometric determination of gold. Lin and Yu[61] applied a procedure similar to that used by Blyum.[60] Sodium tellurite and tin(II) chloride were added to the hydrochloric acid solution of gold; the coagulated precipitate was re-dissolved, nitric acid was removed, and gold determined at the absorption peaks at 551 or 606 mμ. The sensitivity was 2 and 4 times as great as for the Crystal Violet and Methyl Violet methods respectively.

To determine gold in copper, Hirano *et al.*[16] dissolved the metal in a mixture of nitric and hydrochloric acids, evaporated to obtain the chlorides and extracted with ethyl acetate. The method was useful for 2–500 ppm of gold in copper. The authors obtained an error of 10% which they claimed was equal to that of a fire assay, a claim which requires reservations.

Ruthenium and osmium

Chromatographic and solvent extraction methods for the separation of ruthenium from fission products were described by Kiba *et al.*[62] Preliminary chromatographic experiments with nitrosylruthenium-106 trinitrate indicated that there should be oxidation either with bromine to produce ruthenate ions or with hypochlorite to produce perruthenate ions. Furthermore, these experiments indicated that the multicomponent ruthenium species in solution were converted by the bromine or hypochlorite into the simple ruthenium or perruthenate species. Tests with ethanol–butanol–ammonium thiocyanate (50:50:50), glacial acetic acid–water (9:1), pyridine–water (3:2) and isopropyl methyl ketone as solvents indicated superiority of the pyridine solvent. Before use the pyridine was equilibrated with 4*M* sodium hydroxide. The effect of the concentration of the oxidant and of the sodium hydroxide was determined. With the most favourable concentrations extraction was complete only after the solution has stood for 24 hr subsequent to the oxidation. "Antiformin," a solution of active chlorine, sodium hydroxide and sodium carbonate, could be used as the oxidant. The efficiency of the extraction was determined by a measurement of the beta activity of ruthenium-106. The method could be applied successfully to fission product nuclides which accounted for more than 1% of the total activity after the products had been aged for one year.

Kato,[63] in an investigation on the formation and extraction of ruthenium-8-hydroxyquinolinate, obtained findings similar to those of Jasim *et al.*[64] reported several years earlier. Kato applied the tracer ruthenium-106 and provided data on the effects of a variety of extractants, acidity, temperature, time of shaking, buffers, stripping reagents, *etc.* The recommended procedure was closely similar to Jasim's.[64] Essentially complete recoveries were accomplished after heating at 60° for 1 hr at pH 6 and extracting with chloroform or n-butanol. The author's assumption that ruthenium(IV) is the essential oxidation state was based on the use of ruthenium(IV) nitrate and the conversion of ruthenium(III) chloride by air into $Ru(OH)_2Cl_4^-$ and on the incomplete recovery in the presence of hydroxylamine hydrochloride. Aqueous stripping of the quinolinate was accomplished only with concentrated hydrochloric or sulphuric acid. Confidence in the author's data is not encouraged by the method of standardizing. The reliability of the sodium sulphide method[65] was discussed[66] in a report which indicated errors of about 50% for ruthenium.

Kato applied the extraction to the isolation of ruthenium from solutions of fission products. The single interference from zirconium–niobium-95 was eliminated by a nitric acid wash. It was claimed that "Ruthenium-103, -106 of a high radiochemical purity could be obtained from the mixed fission products" by the author's extraction method. In a later paper, Kato[67] used potassium peroxysulphate in a fission product solution made alkaline with sodium hydroxide. Hydrochloric acid and hydrogen peroxide were added, then oxine in acetic acid, and a solution of sodium acetate. After heating at 60° and pH 4 for 1 hr, ruthenium-103, -106 were extracted into benzene. A back-wash with oxalic acid removed ^{95}Zr–^{95}Nb contamination and dilute acid removed the oxine. Ruthenium-103, -106 were stripped with hydrochloric acid. Recovery was 92% in the organic phase and about 70% in the final solution. For the separation of ruthenium(IV) nitrates, nitrosylruthenium(III), and nitritonitrosylruthenium compounds, Bezděk and Menel[68] oxidized with cerium(IV) and periodate in a nitric or perchloric acid medium and extracted the octavalent oxide with tetrachloromethane. The distribution was measured through the activity of ruthenium-106. The period of oxidation, the molar ratio of oxidant, and the acidity and ion concentration of the extracting media were examined for their effect on the extraction. The ruthenium concentrations were about 1–10 μg of metal per ml and the extractions were made at room temperature.

For the extraction of ruthenium nitrosonitrate from nitric acid Nikolaev and Sinitsyn[69] used esters of butylphosphonic acid. There was some evidence that Me_3C groups should provide the highest extraction efficiency.

Aliphatic amines with benzene or hexane were used by Sinitsyn *et al.*[70] for the extraction of ruthenium nitroso pentahalides. Efficiency of extraction increased with increasing amine concentration, with increasing substitution on nitrogen, and with the halogen in the order I, Br, Cl.

For the separation of micro amounts of ruthenium in the presence of iron(III) by extraction of nitrosyl ruthenium complexes with molten naphthols, Konečný[71] investigated the effects of the iron(III) and nitric acid concentrations, and of the amount of naphthol. For the separation of ruthenium he used either a volatilization of the tetraoxide from a permanganate–sulphuric acid solution of the ignited dioxide or an extraction from oxalic acid and hydrochloric acid.

Busev and co-workers have recorded a series of extractive methods for noble metal separation, the integration of which may well introduce new concepts and approaches to both analytical and refining procedures. In a recent series of papers[72–75] pyrazolone derivatives have been proposed as collective and selective extractants. Diantipyrylpropyl-, and diantipyrylphenylmethane complexes of hexachloro-osmates and hexabromo-osmates were extracted by dichloroethane from aqueous media 1–5*M* in hydrochloric acid. Absorbance could be measured at 346 and 378 mμ, the permitted concentration range being 2–23 μg of Os/ml, and the error achieved for 2 μg/ml was $\pm 10\%$. The method allowed separation of osmium from ruthenium, based on the presence of osmium as $[OsCl_6]^{2-}$ and the conversion of $[RuOHCl_5]^{2-}$, the diantipyrylpropylmethane complexes of which are coextracted by dichloroethane, into the tervalent salt by hydrazine hydrochloride.

Coextraction of tervalent ruthenium increased with the concentration of hydrochloric acid, and with increasing concentration of ruthenium and complexing reagent. The authors avoided significant coextraction of ruthenium with osmium by "using the small excess of reagent which is necessary for ensuring almost complete extraction of $[OsCl_6]^{2-}$", the amount of ruthenium passing into the organic phase causing no significant interference with the absorbance of the osmium species. From hydrobromic acid solutions both quadrivalent and tervalent ruthenium are extracted completely. The authors commendably applied the method to distillates of osmium tetroxide from a sulphuric–chromic acid solution, collecting them in 6*M* hydrochloric acid. Hydrazine hydrochloride or sulphate was added to the distillate and the solution was heated to reduce osmium to the quadrivalent state. Presumably, the authors did not co-distil ruthenium, and thus determine osmium in its presence; solvent extraction methods for separations and determinations of this type would add very appreciably to the usefulness of the procedure. Data were included to indicate the absence of interference from iridium and rhodium. Platinum and palladium interfered.

Rhodium and iridium

For the separation of rhodium from iridium Wilson and Jacobs[76] used tributyl phosphate. The method involves conditions which significantly restrict its general usefulness. Aside from failure to provide for the determination of iridium there are inconvenient limitations on the concentrations of both rhodium and iridium. To circumvent this difficulty the authors recommend two procedures, one of which is used for 60–200 μg of rhodium, and the other for 20 μg or less. The permissible limit of iridium for both procedures was 1 mg. The procedures require adjustment to 6–7*M* in hydrochloric acid, treatment of the sample with hydrogen peroxide to oxidize to iridium(IV) and addition of tributyl phosphate, previously equilibrated with hydrochloric acid. Two extractions were recommended. The colour reagents were *N*,*N*′-bis(3-dimethylaminopropyl)-dithio-oxamide and *p*-nitrosodimethylaniline, the former for the 60–200 μg range and the latter for 1·5–25 μg.

A simple and rapid extraction method for the separation of 10–100 μg of rhodium and 7·5–73·8 μg of iridium involves the formation of the tin(II) bromide complex in a perchloric–hydrobromic acid medium and extraction with isopentyl alcohol.[77] Single extractions were sufficient except for larger amounts of rhodium. The use of 200 μg of rhodium resulted in 5 μg or more remaining in the aqueous phase, in which case a second extraction was necessary. The aqueous phase containing the iridium was heated to 99° and the absorbance of the tin(II) bromide complex was measured at 403 mμ. The absorbance of the rhodium complex in the organic phase was measured directly. Large amounts of sodium chloride could be tolerated. For the amounts of rhodium and iridium recommended, absorbance measurements were made between 80 and 140 min after mixing the reagents. Over this period the yellow rhodium complex was stable. The authors believed that the proposed method was faster and simpler than others.

For the isolation of 0·1 mg or rhodium in the presence of up to 100 mg of iridium, Fedorenko and Filimonova[78] used piperidinedithiocarbamate to precipitate rhodium selectively from nitrite solutions of rhodium and iridium. The yellow flakes were then extracted repeatedly with dichloroethene. A 15–60-fold excess of the carbamate, based on the rhodium content, increased the coextraction of iridium from 0·02 to 0·10 mg. The extract was evaporated, and the residue was treated with a solution of hydrogen peroxide and nitric acid to decompose organic matter. Rhodium was then converted into

the chloride. The proposed procedure can be considered a method of separation only insofar as the final determination of rhodium is not affected adversely by the presence of small amounts of iridium. The authors used the tin(II) chloride and polarographic methods for determination.

For the separation of microgram amounts of iridium from milligram amounts of rhodium in 0·1*M* hydrochloric acid solutions Fok[79] extracted tetraphenylarsonium chloroiridate with chloroform containing 1%w/v of tetraphenylarsonium chloride. Iridium in the organic phase was determined spectrophotometrically. Small amounts of platinum, osmium, and palladium could be tolerated. The dissociation constant and solubility product of R_2IrCl_6 in 0·10*M* hydrochloric acid were determined.

For the separation of rhodium from chloride solutions of platinum, palladium and iridium in milligram amounts Busev *et al.*[72,75] used diantipyrylpropylmethane in dichloroethane, extracting from 1*M* hydrochloric acid solution. The technique involved evaporation of the solution of metal chlorides in the presence of sodium chloride, dissolution in concentrated hydrochloric acid and a second evaporation in the presence of hydrogen peroxide, repeated three times. The final residue was dissolved in 1*M* hydrochloric acid and 20 ml of the aqueous phase were extracted with 10 ml of the organic extractant. Stripping from the organic phase was carried out thrice, this operation being repeated before each successive extraction. After separation, the rhodium was found to be spectrographically pure; with the remaining metals a large number of extractions were required to remove spectrographic traces of rhodium. The amounts of metals used by the authors are within the range of gravimetric methods and beyond the recommended range for most extractive spectrophotometric methods for the noble metals. A comparison of the time required for single and for multiple determinations, including the actual working time and the standing time, would be of some interest.

Busev and Akimov[72,75] also used diantipyrylpropylmethane for the separation of platinum, palladium, and rhodium from iridium and the spectrophotometric determination of iridium. As recorded above,[74] osmium(IV) and ruthenium(IV) are similarly isolated by the dichloroethane extractant. Busev[72] stated that 5–6% of the rhodium present is simultaneously extracted. However, "rhodium is not extracted from solutions which have been boiled or allowed to stand", and furthermore, the degree of separation from rhodium increases with increasing hydrochloric acid concentration. However, the procedure given for the separation of iridium from rhodium fails to incorporate these favourable factors. It is stated that under certain conditions of acidity and rhodium and reagent content, the absorbance of the coextracted rhodium complex is negligible at the wavelength of 498 mμ used for iridium determination. The method is applicable over ranges of 40–350 μg of iridium and 1–4 mg of rhodium. The preparation of the chloride solution for extraction required evaporation in the presence of sodium chloride, addition of hydrogen peroxide, and complete conversion into $[IrCl_6]^{2-}$. Data were recorded for iridium to rhodium ratios from 1:3 to 1:108.

For the separation of rhodium from platinum, palladium and iridium, Borbat *et al.*[80] treated the chloride solutions of the metals with tri-isobutylamine hydrochloride and extracted with chloroform. Three extractions were made from 0·3*M* hydrochloric acid. Presumably, the reaction follows an ion-exchange mechanism. Copper and iron could be removed from the organic layer containing the platinum, palladium and iridium, by washing with 0·1*M* hydrochloric acid.

Palladium and platinum

Solvent extraction studies of addition compounds of palladium halides with triphenylphosphine, -arsine and -stibine have been made.[81,82] Triphenylarsine in cyclohexane extracts palladium from weakly acidic media containing excess of iodide and sulphite. The latter prevents interference from platinum, which in excess adversely affects the separation of palladium. However, an increase in acidity encouraged the formation of sulphur dioxide with resulting mechanical losses; excesses of iodide or reagent accelerated the simultaneous extraction of platinum.

Tri-n-octylamine reacts with palladium tetrachloropalladate to form an exchange complex extractable with toluene. Mazuyova and Gindin[83] determined the effect of varying concentrations of hydrochloric acid, lithium chloride, amine reagent and palladium salt on the separation.

Isobutyl methyl ketone was used to extract the palladium iodide complex from sulphuric acid solutions of niobium and zirconium.[84] A 10% excess of potassium iodide and 20% v/v sulphuric acid were used for amounts of palladium of up to 1 mg/ml. The presence of chloride encouraged the coextraction of niobium and zirconium.

Thiocyanate and halide complexes have been used for the extraction of palladium and its separation from silver. Golub *et al.*[85] determined the distribution coefficients in various concentrations of alcohols and cyclohexanone in benzene. Palladium could be separated from silver by dissolution with nitric acid and extraction with amyl alcohol. Methods such as these could probably be applied effectively to determine palladium in silver assay beads and other silver–palladium alloys.

For the extraction of microgram amounts of palladium in the presence of large proportions of rhodium, nickel, cobalt and manganese, Ziegler and Pape[86] used methylene to extract the complex of dimethyl ether with tetraiodopalladate(II), the absorbance of which was measured at 340 mμ.

Undue exposure to daylight reduced the absorbance rapidly. Interference from platinum, iridium, copper and iron required a separation, and the previously recorded silver sulphite–cellulose method was recommended.

A more generally useful method for the separation of palladium was also described by Ziegler *et al.*[87] and allows a separation from 1000-fold quantities of platinum and large excesses of iron, cobalt, nickel, copper and chromium. In the presence of gold in ratios from 1:10 to 1:40 there are positive errors increasing from 0·9 to 2·0%. Phenylacetylene or isopropenylacetylene forms palladium complexes, extractable by methylene chloride to give solutions with an absorption maximum at 317 mμ. The procedure involved an adjustment to pH 1–4 and addition of a 10% solution of phenylacetylene in methylene chloride or a similar solution of the isopropenylacetylene. The turbidity which appears after 10–15 min standing clears after a further addition of solvent.

Solvent extraction was used by Eshelman *et al.*[88] for the separation of 5–100 μg of palladium and rhodium chlorides which were then determined flame photometrically. Palladium was first removed by extraction with salicylaldoxime in 4-methyl-2-pentanone, the pH of the aqueous phase being adjusted to 3·2 ± 0·2 with ammonia. Standing for 1 hr with occasional shaking was required. To isolate rhodium the aqueous phase was treated with a 4-methyl-2-pentanone solution of diethyldithiocarbamate. The mixture was shaken and buffered with ammonium acetate to pH 8. Standing for 2 hr and occasional shaking were required.

Useful modifications of the tin(II) chloride determination and extraction of platinum have been recorded. Khattak and Magee[89] investigated the application of high molecular weight amines for the extraction of platinum in the presence of associated base and noble metals. Two procedures were included; one for the separation of platinum from palladium, and the second for the separation from rhodium. The amines recommended were tri-n-hexylamine, tri-n-octylamine and primene, dissolved in chloroform or benzene. The separation from palladium involved the careful addition of ammonia, then concentrated hydrochloric acid and tin(II) chloride solution without delay, extraction, filtration and dilution to volume with pure solvent. Absorbance was measured at 400 mμ.

For separation from rhodium, the chloride solution was treated with the amine, the aqueous layer with the dissolved rhodium was discarded, and platinum in the organic phase was treated with tin(II) chloride.

The sensitivity was five times that of the usual tin(II) method. The high extraction efficiency was indicated by the need for only a single extraction. The complex was stable in chloroform for 2 hr and in benzene for many hr. The molar absorptivity was greater in benzene than in chloroform. The concentration of hydrochloric acid was not criticial, the most suitable range being 1·3–1·5*M*. There was no interference from osmium(IV), ruthenium(IV), iridium(IV), nickel or iron added directly to platinum solutions. The non-interference from palladium is rather surprising. The efficiency of separation depended on the basicity of the solution. One would expect that at a pH as great as 9, with subsequent acidification, the development of the palladium tin(II) chloride complex would be delayed sufficiently for platinum to be separable but one would also expect that there would be a rapid development of the platinum ammonia complex which on acidification would resist conversion into the tin(II) complex. The authors emphasize the need for the careful timing of 0·5–1 min between the addition of ammonia and the acidification. The data obtained indicated that for a 5-min delay the error was 37·5 μg in 100 μg of platinum. In the present author's opinion, complexing of the platinum by ammonia is initiated immediately on addition of ammonia and this possibility would undoubtedly limit the general usefulness of the separation, particularly with small concentrations of the metals. Coincident with this effect one may expect high results with relatively high proportions of palladium to platinum, and this effect is made clear by the authors' statements and data. One notes also that the method of separation does not include a subsequent determination of palladium and here again it would seem that the associated species do not lend themselves to a direct colorimetric determination of palladium.

Hydrochloric acid solutions (0·1*M*) containing sodium thiocyanate and platinum, irradiated for 15 min with a 500-W incandescent bulb, react with triphenylisopropylphosphonium chloride to produce a yellow complex which can be extracted with a variety of solvents. Senise and Pitombo[90] developed this method for separation of platinum from other noble metals. Separation from palladium involved irradiation of the metal solution containing excess of thiocyanate, addition of the triphenylisopropylphosphonium chloride to form the platinum complex and to precipitate the palladium complex, and extraction of the former with ethyl acetate. The precipitated palladium complex in the aqueous phase was then extracted with cyclohexanone. With large proportions of palladium and 100–500 μg or less of platinum per ml, palladium was precipitated prior to irradiation because the intense colour of its complex interfered with the irradiation required for the platinum thiocyanate reaction. The authors preferred the use of light to catalyse the reaction rather than heat which is normally used to hasten the thiocyanate reaction. With heating the authors experienced greater difficulty in achieving acceptable accuracy and precision. Irradiation for 15 min with a 500-W incandescent bulb (distilled water being used as light-filter) was found satisfactory. Bright

sunlight or ultraviolet radiation could also be applied. For 50–500 μg of platinum an exposure of 5 min was sufficient but for smaller amounts of platinum, and in the presence of foreign constituents, longer exposures were required. Isobutyl methyl ketone or tri-n-butyl phosphate could be used as solvents by coextracted small amounts of palladium. Surprisingly, the ethyl acetate extractions must be made in diffuse light, because although light was required to catalyse the formation of the platinum thiocyanate complex, the colour faded during the extraction. Absorbance was measured at 365 mμ and the optimum range was 5–20 ppm. The compositions of the two complexes were $[(C_6H_5)_3C_5H_7P]_2$-[Pt or $Pd(SCN)_6$]. Palladium was determined by measuring the absorbance of the cyclohexanone phase at 345 mμ for 10 ppm and at 410 mμ for higher concentrations. Despite the authors' conclusion that the palladium cyclohexanone solution was "not very favourable for precise determination" the data provided indicated results in which the precision and accuracy were about those obtained for platinum. It would seem that this aspect of the separation requires further exploration. Separations of platinum were successful for solutions containing rhodium and iridium, the latter requiring reduction by ascorbic acid: there was some interference from ruthenium in amounts greater than 200 μg. Gold could be removed by prior precipitation and removal with benzene. Silver did not interfere.

Derivatives of dithiocarbamic acid as separatory reagents for platinum and palladium were investigated by Pyle and Jacobs.[91] The dibenzyl derivative in chloroform solution was preferred. The procedure required the addition first of sulphur dioxide, then hydrochloric acid if platinum was present, followed by two extractions with chloroform. The organic extract was ashed prior to determination of platinum and palladium. Rhodium interfered seriously with the simultaneous determination of these two metals. For amounts of about 25 mg of the two metals there was little interference from 0·5 mg of iron and nickel. Relatively, the method has little to recommend it; the ashing technique is laborious, and in any case, further researches ought to be completed before the value of the method can be properly assessed. The authors' statement that the "reagents were used without further purification" suggests that some effort was made to ensure the purity of the reagents although no confirmatory data were included. One would hope that such investigations would include a directed effort to ensure purity of reagents.

To determine platinum metals in silicate rocks by a spectrochemical method Hahn-Weinheimer[93] decomposed a few g of sample by an alkaline fusion. An aliquot of the solution of the fused sample was treated with hydroxylamine hydrochloride at pH 3·5 while nitrogen was passed through it. Following the addition of hydrochloric acid the 2-quinolineselenol reagent was added and repeated extractions were made with chloroform. The latter was volatilized and the residue was wet-ashed at 500° with the addition of magnesium nitrate and nitric acid. The claim that losses of osmium were thus avoided most certainly requires confirmation. The resulting residue was then added to a carbon electrode and spectrochemical determinations were made by standard techniques. The detection limits in ppm for each metal were for osmium 2, iridium 0·05, ruthenium 0·05, rhodium 0·05, platinum 0·01 and palladium 0·01. The technique was insufficiently supported by experimental evidence.

For the study of the complex equilibria involved in the hydrolysis of haloplatinates Davidson and Jameson[92a] used the complexes formed with liquid anion-exchangers *e.g.*, Amberlite A-2, extracted by organic solvents. The results of extractions from hydrolysed haloplatinates indicated that the only platinum species extractable into LA-2/cyclohexane was the hexahaloplatinate ion, extraction of hydrolysis products being poor. The extraction behaviour was interpreted as a simple ion-exchange only for fresh haloplatinate solutions in the presence of the corresponding halide.

Multicomponent systems of noble metals

Various extractive and determinative procedures for platinum, palladium, rhodium and iridium were modified and integrated by Faye and Inman[89] to provide general methods for the determination of microgram amounts of these metals. The platinum and palladium iodide complexes were isolated simultaneously and selectively removed by two extractions with tributyl phosphate (TBP) in hexane followed by three aqueous extractions with concentrated nitric acid. For the separation of 50 μg or more of palladium, aliquots of the nitric acid extract were used and platinum and palladium were separated and determined with *p*-nitrosodimethylaniline by a procedure based largely on the early work of Yoe and Kirkland.[94] The aqueous extract from the tributyl phsophate separation contained the rhodium and iridium, which were then converted into the chloro salts; rhodium was separated as described by Wilson and Jacobs[76] and determined spectrophotometrically by the tin(II) bromide method of Berman and Ironside.[95]

Faye and Inman[89] extended the Wilson and Jacob separation by extracting iridium from the TBP-hexane phase with hydrobromic acid and determining it with tin(II) bromide as described by Bermah and McBryde[96] except that phosphoric acid was added to improve the precision. Extractions from the iridium-TBP-hexane phase could also be accomplished by hydrochloric or perchloric acids.

Initially, samples of the four metals were prepared for separation by evaporation in the presence of sodium chloride and treatments with 12*M* hydrochloric acid and 30% hydrogen peroxide followed by evaporations. The data indicated acceptable recoveries over a range of concentrations and ratios of one metal to another.

A theoretical and useful approach to the solvent extraction and determination of platinum metals was introduced by Forsythe, Magee and Wilson.[97] These authors prepared extractable pyridine-thiocyanate complexes of palladium and ruthenium; the composition of the former was $PdPy_2(SCN)_2$, and ruthenium probably formed anionic complexes with ratios of thiocyanate to ruthenium determined by the relative concentration of thiocyanate. The dissolved constituent $[Ru(H_2O)Cl_5]^{2-}$ in acid solution presumably formed crimson $Ru(SCN)_4^-$ or $Ru(SCN)_5^{2-}$. The latter on being heated sufficiently, and particularly at high pH, formed a blue constituent, $Ru(SCN)_4^{2-}$ or $Ru(SCN)_3^-$ as a result of reduction to bivalent ruthenium by the thiocyanate ion, catalysed by the metal. Hexone was used to extract the yellow palladium complex at pH 11–12. Two extractions were sufficient and the absorbance was measured at 345 mμ. The basic aqueous solution from the palladium–hexone extraction was acidified with concentrated hydrochloric acid and the blue ruthenium complex was extracted with hexone and its absorbance measured at 570 mμ. The minimum amounts of metals were 25 μg. The upper limit was not stated.

Perhaps the most surprising aspect of this procedure is the success achieved in making the acidic palladium solution strongly alkaline and in acidifying the strongly basic ruthenium solution without significant formation of hydrated oxides, which, particularly in the case of ruthenium, are not always readily redissolved in excess of acid or base. Presumably, the authors encountered some difficulty as indicated by their stressing the necessity of a rapid addition of acid or base.

In an associated publication[98] dealing with the separation of rhodium, palladium and platinum, pyridine was used instead of the concentrated sodium hydroxide solution, to adjust the pH to 6·0–6·5, forming the complex $PdPy_2(SCN)_2$. Hexone was again used as extractant followed by adjustment of the aqueous phase to pH 2·0–2·5 with hydrochloric acid, heating to 90° for a period of 4 min and subsequent extraction with hexone. Absorbance was measured at 385 mμ. The yellow aqueous phase from the platinum extraction was adjusted to 3–4*M* in hydrochloric acid. Hexone was used again to extract the rhodium, the absorbance of which was measured at 380 mμ. The lower limits of concentration were 25 μg of palladium and 50 μg each of platinum and rhodium. The results indicated an upper concentration of about 250 μg/20 ml.

An interesting sequential series of extractions of constituents of noble and base metal alloys was described by Senise and Pitombo.[99] The method is based on the application of a variety of solvents for the selective removal of metal complexes formed with triphenylisopropylphosphonium salts and excess of thiocyanate. Thus chloride solutions containing large proportions of gold together with iron(III), silver, copper(II), platinum(IV) and palladium(II) were treated with toluene or benzene as extractants to produce the following solutions: gold (orange), iron with tri-n-butylphosphate (red), silver with 2-methylcyclohexanol (colourless), platinum with tri-n-butylphosphate at 65–70° (yellow), copper with isobutyl methyl ketone (wine-red), and palladium with cyclohexanone (yellow). The order of extraction must be as indicated. The same principle was applied to gold alloys which were dissolved in *aqua regia* containing sufficient hydrochloric acid to dissolve silver. Because the extractions were essentially quantitative one would hope that some effort will be made to apply the approach to silver alloy beads obtained from fire assay treatement. Methods such as these could be of considerable value when modified to provide field tests or even quantitative procedures.

An interesting approach to the selection of separatory reactions for the noble metals was discussed by Gindin *et al.*[100] It was assumed that because quaternary ammonium bases were relatively basic compared with the amines previously used by these authors, there would be a lesser tendency to form co-ordination complexes with the noble metals, thus encouraging more effective extraction. The salts of alkylbenzyldimethylammonium chloride and dialkyldimethylammonium chloride proved to be promising reagents when used with 1,2-dichloroethane (containing a little aliphatic alcohol) as solvent. The order of ease of extraction from low hydrochloric acid concentration was Pt(IV) > Pd(II) > Ru(III) > Ir(IV) > Rh(III) > Ir(III). As would be expected, the complex salts formed with the organic bases produced relatively insoluble salts with platinum and iridium. The authors stated that "the solubility of the platinum-metal complexes is much higher when the nitrogen atom is at the centre, and not at the end, of the hydrocarbon chain." It was noted also that an increase in the number of carbon atoms in the quaternary compounds sharply increased the distribution coefficients of these compounds. The authors' comments and data were of a general nature and experimental analytical data would be a welcome addition.

A fundamental study of the benzene extraction of the dithizonates of gold, platinum, palladium, silver, *etc.* was made by Kawahata *et al.*[101] The ranges of pH and sulphuric acid concentrations required to achieve 100% recovery were determined. Excesses of dithizone were removed by washing with dilute alkali solutions. The molar absorptivities on the complexes in benzene solution were determined. As a solvent benzene was superior to chloroform or carbon tetrachloride. The acidities

required for maximum extraction were <15*N* and <pH 5 for palladium; 1·0–10·5*N* for platinum(II); >7*N* for gold.

Berg and Lau[102] used a countercurrent technique to separate some of the platinum metals. Berg's earlier work[103] dealt with the feasibility of extracting the chloro-complexes of platinum and palladium, platinum and rhodium, rhodium and iridium. This new work[102] involved extractions with tributyl phosphate of thiocyanate complexes of the platinum metals. Recoveries of platinum, palladium, rhodium and iridium were 93–97%. The method of separation involved evaporation and dissolution in a hydrochloric acid and potassium chloride buffer at pH 1. Solid potassium thiocyanate was added to provide a 10:1 mole ratio of thiocyanate to metal. The sample was heated, cooled, and transferred to the first tube of a Craig extractor. The distribution coefficients for palladium, platinum, rhodium and iridium were 139, 62·3, 0·19 and 0·09 respectively. The procedure provided a separation of platinum and rhodium, platinum and iridium, palladium and rhodium, and palladium and iridium in less than 10 stages.

Jasim *et al.*[64,104] used solvent extractions to separate and determine the six platinum metals. The first procedure was developed to separate ruthenium, rhodium and palladium from solutions containing only these metals. In each case chloroform was used as the solvent and the determination required a measurement of the absorbance of the 8-hydroxyquinoline complex; ruthenium at 410 mμ, rhodium at 425 mμ and palladium at 450 mμ.

From the recovery data the concentrations were about 5–100 μg/ml for palladium, and 10–100 μg/ml for ruthenium and rhodium. The procedure[64] involved adjustment to 0·1*M* in hydrochloric acid, addition of triphenylmethylarsonium iodide and sodium chloride solution and a chloroform extraction. The organic extract was then treated with oxine and chloroform to form the palladium oxinate. The aqueous phase from the palladium triphenylmethylarsonium extraction was treated with oxine in chloroform, the pH adjusted to 6·4 with sodium acetate, and ruthenium in the organic layer was combined with the residual ruthenium from the rhodium solution, and its absorbance measured. The aqueous extract from the ruthenium separation contained the rhodium, and was treated with butylcellosolve to remove the residual ruthenium; the butylcellosolve was then treated with a chloroform solution of oxine which was then combined with the main ruthenium fraction. The aqueous layer containing the rhodium was heated with oxine in acetic acid, the pH being adjusted to 6·0–8·0 with ammonium acetate, and was then heated and cooled, and the rhodium was extracted by a chloroform–oxine solution. Possible interferences from osmium, iridium and platinum were not discussed except that they did not interfere with the determination of ruthenium; this characteristic could find application in the separation of osmium from ruthenium.

Separation of the metals of the second triad were discussed in the second paper.[104] Osmium was first isolated by a chloroform extraction following colour development with pyrocatechol at pH 3 and subsequent heating. The blue chloroform layer was used for absorbance measurements at 595 mμ. Platinum in the aqueous layer was extracted with isobutyl methyl ketone which was then evaporated, and the residue was treated with nitric, sulphuric and perchloric acids. Thiosemicarbazide was added followed by sodium carbonate, and amyl acetate as the extractant. The resulting blue layer was treated to allow the determination of platinum with tin(II) chloride. The aqueous layer from the platinum extraction was treated to determine iridium volumetrically by hydroquinone in the presence of 3,3′-dichlorobenzidine as indicator. The method was used for osmium over the range of 6–100 μg/ml, for iridium 12–100 μg/ml and for platinum 7–100 μg/ml.

The application of isoamyl alcohol as an extractant for the tin(II) bromide complexes of platinum, rhodium, palladium, iridium and gold in microgram amounts was described by Pantani and Piccardi.[105] In the case of gold a precipitate was formed which required the addition of gelatin to encourage homogeneity but the gold complex was not extractable with the alcohol. In any case, a separation of gold from platinum could be accomplished by extraction of a complex aurate with ethyl ether or isoamyl alcohol, and followed by an extraction of the platinum–metal tin bromide complexes. Because the iridium–tin bromide complex does not form at room temperature its separation from the complexes of platinum, rhodium, and palladium could be thus affected. In this case the isoamyl alcohol was used with the metal solutions in perchloric and hydrobromic acids containing tin(II) bromide. For the separation of platinum from rhodium and palladium the latter is first removed selectively by extraction of the α-nitroso-β-naphthol complex into amyl alcohol. However, the results were 5–7% low. A spectrophotometric method for the simultaneous determination of rhodium and platinum was described.

Zusammenfassung—Diese Übersicht handelt von den Trennungen der sieben Edelmetalle durch Ionenaustausch und flüssig-flüssig-Extraktion, die zwischen den früheren Übersichten und Januar 1966 publiziert wurden. Die in Lösung vorliegenden Edelmetallspezies werden diskutiert, sofern sie zur Trennung und Bestimmung in Beziehung stehen.

Résumé—Cette revue traite des méthodes d'échange d'ions et d'extraction par solvant pour séparer les sept métaux nobles, publiées ultérieurement aux précédentes revues et antérieurement à janvier 1966. On discute des espèces chimiques sous lesquelles les métaux nobles sont présents en solution dans la mesure où elles sont reliées à la séparation et au dosage.

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SPECTROSCOPY IN SEPARATED FLAMES—I

THE USE OF THE SEPARATED AIR–ACETYLENE FLAME IN THERMAL EMISSION SPECTROSCOPY

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Summary—The separation of a premixed air–acetylene flame is described. The interconal zone of this flame exhibits very low radiative background, and is only slightly cooler than that of a normal air–acetylene flame. The use of the separated flame in flame photometry, for which it has several pronounced advantages, has been investigated.

IT is well known that premixed hydrocarbon–air flames consist of two separate reaction zones, *i.e.*, the primary reaction zone where the combustible gas mixture burns principally to carbon monoxide, hydrogen and water, and an "outer mantle" or secondary diffusion flame where the hot gases burn with atmospheric oxygen to carbon dioxide and water. The hottest part of flames of this type is normally in the centre of the flame immediately above the primary zone. The existence of the two reaction zones may be demonstrated by using the flame "separator" introduced independently about 1891 by Teclu[1] and by Smithells and Ingle.[2] In this device the combustible gas–air mixture is made to burn on the top of a circular port fitted inside a wider glass tube which forms an extension above the inner burner port. The lower end of this tube is given an air-tight fitting around the burner stem. The primary combustion can then be made to occur on the inner burner port, while the pale bluish-violet secondary "diffusion" flame is maintained at the top of the outer glass tube. The space between the reaction zones, the interconal zone, is thus extended in length. This dark zone also contains the hottest part of the flame, and can be viewed without interference from radiation produced in the secondary reaction zone which normally surrounds it in unseparated flames. It is the interconal zone of premixed laminar flames which is usually employed in analytical flame spectrophotometry, and it is in this hot region that the atoms of most elements exhibit the strongest emission when introduced into the flame by nebulization of solutions of their salts. To the best of our knowledge the possibility that separated flames might have analytically useful properties has not been investigated. Separated flames might provide "atom reservoirs" with very low radiative background for analytical purposes, and their use could prove advantageous in emission flame photometry as well as in atomic absorption and atomic fluorescence spectrophotometry.

Smithells and Ingle[2] reported the separation of low burning-velocity air-supported flames of coal-gas, ethylene, methane, pentane, heptane, and benzene burning at an open Bunsen-type burner port. We achieved separation of flames of coal-gas or ethylene with air at a burner port of this type, but decided that a flame of higher temperature was required for flame photometry. This requirement is filled by the air–acetylene flame, but because of its high burning-velocity it is difficult to maintain

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at an open circular burner port*. This paper reports the separation of a premixed air–acetylene flame at a commercially available Meker-type flame photometer burner head and gives a preliminary report of its utility in emission flame photometry.

EXPERIMENTAL

Apparatus

A Hilger large quartz spectrograph was used to make qualitative identification of the radiating species in the flames. Quantitative measurements of the intensity of the radiation from the flames were made with a Unicam SP 900A flame spectrophotometer fitted with a Sargent recorder. An SP 900A stainless steel burner stem, acetylene emission head and acetylene jet were employed.

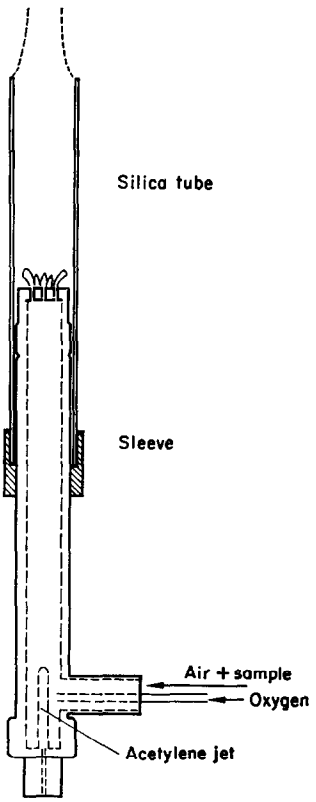

FIG. 1.—Diagram of burner arrangement employed.

Provision was made for the enrichment with oxygen of the air used for aspiration at the junction of the air inlet with the burner base (see Fig. 1). Samples of aqueous solutions were introduced into the flame *via* the Unicam indirect nebulizer and cyclone expansion chamber.

Flame separator

This study was made with a premixed air–acetylene flame which was "separated" by fitting a "Vitreosil" transparent fused silica tube, 20 mm internal bore and 12 cm long, on to the Unicam Meker type burner *via* an air-tight sleeve, enabling the silica tube to be adjusted vertically to provide variable "separating" distances. Between 6 and 8 cm was found to be a convenient distance between the top of the stainless steel burner head and the upper edge of the silica tube. The Unicam burner head has thirteen orifices of *ca.* 1·2 mm diameter arranged in a square of side 9 mm. With this arrangement as shown in Fig. 1, the flame is easily separated into a stable primary zone consisting of 13 separate

* Mavrodineanu[4] reports the separation of an air–acetylene flame at a Lundegårdh-type burner, and its use to illustrate excitation mechanisms.

cones on the burner head inside the silica tube, and a secondary diffusion flame burning at the top of the silica tube. Stable separated flames are obtained over a fairly wide range of fuel–air mixture strengths, as shown in Fig. 2. The flame tends to become turbulent and noisy with very lean mixtures, and the use of very rich (luminous) mixtures leads to the deposition of carbon on the inside walls of the silica tube. Turbulent noise also occurs when a silica tube of very wide diameter is used, or when the distance between the burner head and the upper edge of the silica tube is increased to more than 8–10 cm. This separator arrangement was employed with both air–acetylene flames and oxygen-enriched air–acetylene flames. Without alteration of the arrangement for air–acetylene, the air used

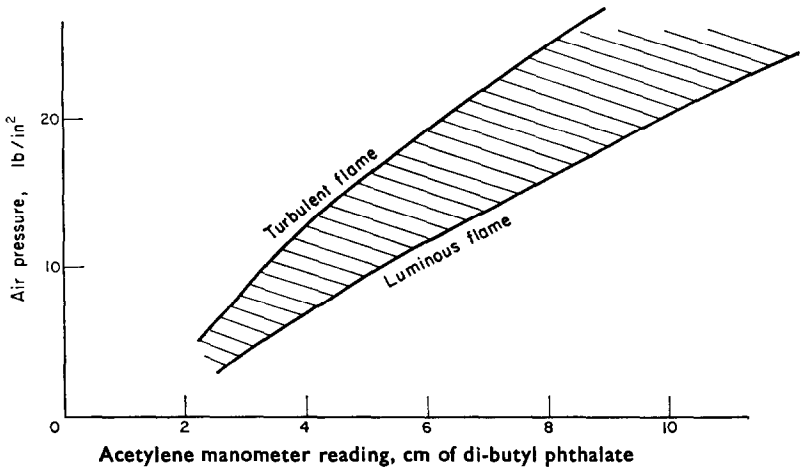

FIG. 2.—Effect of air pressure and acetylene flow-rate on stability of the separated flame.

for nebulization may be enriched by the addition at the burner base of as much as 15 volumes of oxygen to every 100 volumes of air. The acetylene flow-rate must, however, be increased to obtain a stable flame when oxygen enrichment is used. Attempts to use air enriched with more than *ca.* 15% of oxygen with this burner arrangement lead to turbulence and possible blowing back of the flame owing to the greatly increased burning-velocity of the enriched gas mixtures.

RESULTS

Flame emission characteristics

The primary zone of premixed air–acetylene flames radiates strongly over much of the visible and near ultraviolet region of the spectrum, exhibiting the molecular band spectra of C_2, CH, and OH as well as the strong CO continuum. Because of this intense background radiation the primary zone is seldom used in analytical flame photometry. The radiation from the secondary diffusion zone constitutes the main flame background in the premixed flames commonly employed in flame photometry. The emission spectrum from this zone in the air–acetylene flame burning as a diffusion flame at the top of the separator shows only the CO continuum due to the reaction $CO + O \rightarrow CO_2 + h\nu$ which persists over much of the visible region, and the strong OH band systems in the near ultraviolet with heads at 2811 Å and 3064 Å. Figure 3 shows a comparison, at the same air and acetylene flow-rates, of the background emission spectrum from the interconal zone of the separated flame with the spectrum of an unseparated air–acetylene flame. When the separator is used, the background radiation from OH and CO in the interconal zone is at least two orders of magnitude lower than in the unseparated flame. The very weak band emission which appears in the visible region (Fig. 3) is probably due to imperfect shielding of the primary cones

from the slit of the spectrophotometer. Figure 3 also shows how the intensity of this band emission depends on the fuel:oxidant ratio.

Emission from elements in separated flame

When nebulized solutions of metal salts are introduced into the separated flame, most of the atomic line emission takes place in the interconal zone. The emission intensity is greatest in the hottest part of the flame just above the tips of the primary

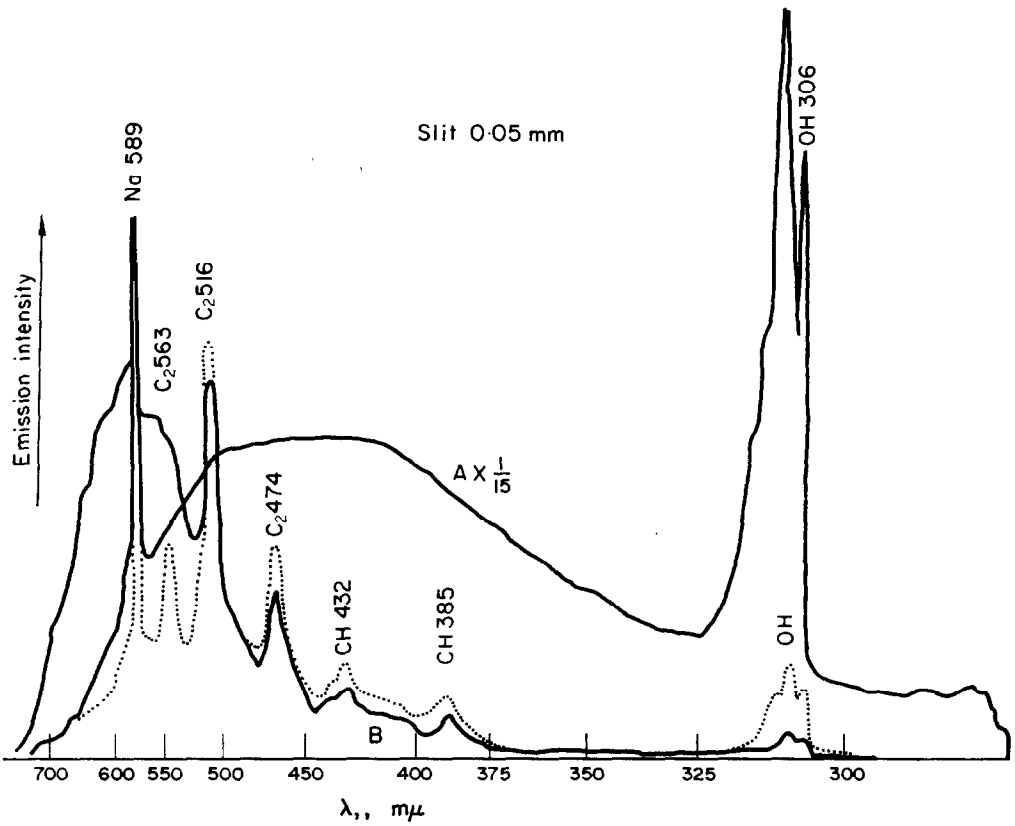

FIG. 3.—Background emission from unseparated (*A*) and separated (*B*) flame. The ordinate of A should be multiplied by 15 to compare absolute intensities. Dotted line shows effect of decreased fuel flow-rate on emission spectrum from separated flame.

cones. For the elements investigated, however, we have found that the intensity of emission from the separated flame is weaker than from a similar unseparated flame. The intensities of the thermal emissions for the elements investigated in the separated flame relative to their emission in the unseparated flame are shown in Fig. 4. Even though the observed intensities are lower, the analytical signal to background ratio is very considerably increased. There is no doubt that some loss of intensity is caused by absorption and reflection losses at the silica walls of the tube. The principal reason for the decreased emission observed, however, is that the interconal zone of the separated flame is slightly cooler than in an unseparated flame. This is caused by

the absence of the surrounding diffusion flame which normally provides heat by the reaction

$$CO + O \rightarrow CO_2 + 67{\cdot}6 \text{ kcal.}$$

The curves shown in Fig. 4 show the relative emission one would expect for a flame 20°, 30° and 40° cooler than the stoichiometric air–acetylene flame ($T = 2325°$) assuming that the emission is wholly thermal (*i.e.*, proportional to $e^{-E/kT}$), and the concentration of neutral atoms is unaffected by this slight temperature drop. The assumption of a constant ground-state atom concentration is known not to be strictly

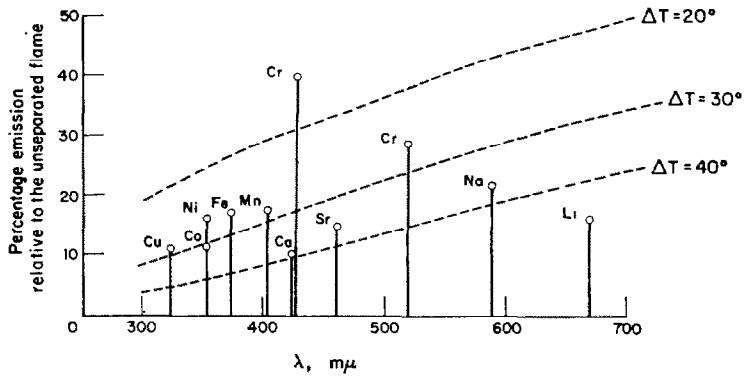

FIG. 4.—Emission intensities for elements in the separated flame compared with their emission in the unseparated air–acetylene flame at the same fuel and air flow-rates.

valid for elements forming stable hydroxides such as calcium and lithium, but suffices to a first approximation. The loss of intensity can then be explained if the separated flame is effectively only about 30° cooler than the ordinary flame immediately above the primary cones. We have observed also that the emission from the flame relative to that of an unseparated flame also depends on the spraying rate of the sample, and is favoured by decreasing the spraying rate. This suggests that the heating capacity of the separated flame may be less than that of the ordinary flame, and this may be an important factor contributory to the decreased emission intensity. The relative emission from the chromium triplet at 4254 Å is very much greater than expected from the general pattern of results shown in Fig. 4, whereas the emission from the chromium triplet at 5206 Å agrees with the results for the other transition elements. It is possible that the chromium emission at 4254 Å is partly supra-thermal in origin. This supra-thermal emission may result from a direct energy transfer reaction involving excited CH molecules and chromium atoms. Two of the three lines in the blue chromium triplet can be shown spectrographically to be virtually coincident with rotational lines within the CH band at 4315 Å [$^2\Delta - {}^2\pi(0, 0)$].

The variation of intensity of emission with the height of observation has been studied for several elements in the separated flame. This was achieved by placing a horizontal slit in front of the spectrophotometer entrance slit and adjusting the burner assembly vertically in front of the horizontal slit. Figure 5 shows the dependence of the emission intensity on the height of observation for calcium, sodium, lithium and chromium at 4227, 5890, 6708 and 4254 Å respectively. The emission profile for calcium at 4227 Å in an unseparated flame under similar mixture conditions is also shown. Other elements exhibit similar emission profiles after allowance is made for

differences in excitation energies and chemical behaviour. Owing to the absence of the surrounding diffusion zone, the emission intensities decrease much more rapidly with height in the separated flame than in a normal flame. The hottest part of the separated flame, where maximum emission is observed, is also relatively independent of the mixture strength, and is invariably immediately above the reaction zone. This may be contrasted with the unseparated flame where the height of maximum emission varies markedly with the fuel–air conditions employed. There is thus no

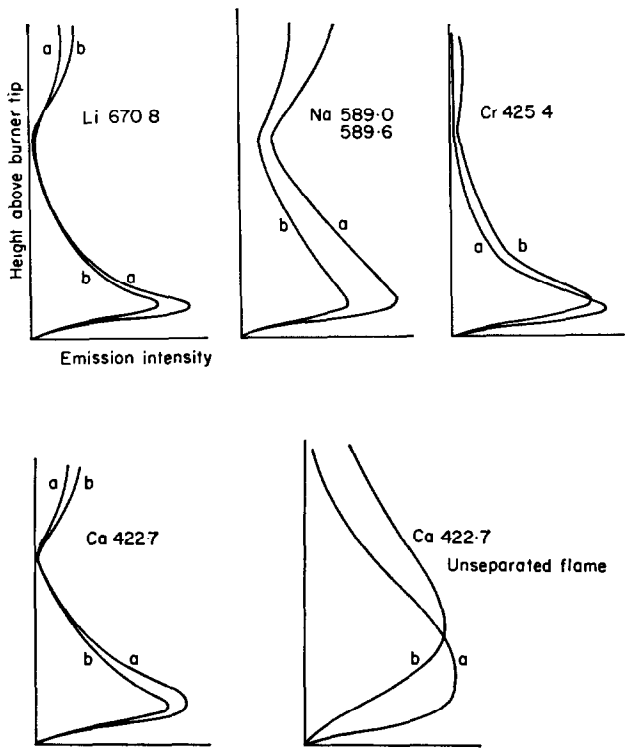

FIG. 5.—Variation of emission intensity for some elements with height of observation; (*a*) fuel-lean and (*b*) fuel-rich flames. The corresponding height profiles for calcium in the unseparated flame is also shown.

need with the separated flame to vary the height of observation according to the mixture used. The emission profiles (as a function of height) of fuel–rich separated flames are observed to be slightly steeper than those of lean flames, and the lean flame is slightly hotter immediately above the reaction zone, and gives more intense emission for several elements than the fuel–rich flame in this region.

Methods of improving sensitivity

The fact that the interconal zone of the separated flame is slightly cooler than that of an unseparated flame represents a disadvantage in its use in flame emission spectrophotometry. The small drop in temperature, while relatively unimportant in atomic absorption or atomic fluorescence spectroscopy, results in a depression of the intensity of thermal emission of elements introduced into the flame. The lowering in emissivity

is not a very great disadvantage, however, since it is never greater than one order of magnitude, but nevertheless we have investigated several methods of restoring the emission intensities to their values in unseparated flames.

The silica tube may be coated externally with magnesium oxide, which acts as a diffuse reflector, and a slot can be made in the coating facing the spectrophotometer entrance slit. With this device it is possible to double the sensitivity for calcium and other elements, and thus to restore much of the lost sensitivity.

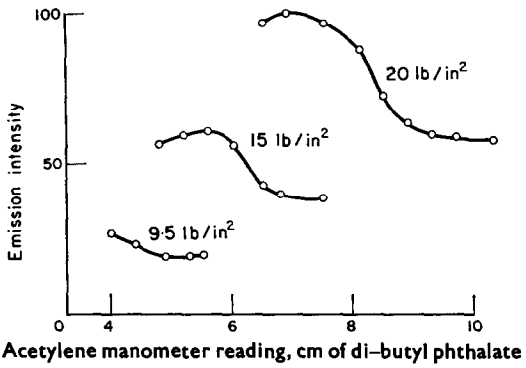

FIG. 6.—Variation of emission intensity for calcium at 4227 Å with air (nebulization) pressure and acetylene flow-rate.

A more useful method of increasing the sensitivity is to increase the flame temperature by enrichment of the air–acetylene mixture with oxygen. The oxygen may be introduced at the burner base where it is bled into the air used for sample nebulization. This oxygen-enriched air then mixes with the acetylene in the burner stem. The addition of only 15% of oxygen (by volume) to the air from the nebulizer results in a sufficient rise of flame temperature to increase the calcium emission at 4227 Å twenty-fold. This represents a considerable improvement in sensitivity for calcium over the original unseparated flame sensitivity, and although the radiative background is slightly greater, the higher emission to background ratio for the line is still retained. This thus constitutes an advantage over an unseparated flame similarly enriched with oxygen.

The utility of the oxygen-enriched separated air–acetylene flame can be demonstrated from a study of the emission of magnesium at 2852 Å and bismuth at 3068 Å In the unseparated flame it is difficult to identify the magnesium 2852 Å resonance line in emission for low concentrations of magnesium (below 100 ppm) because this line is obscured by the emission from the OH system with a head at 2811 Å. In the separated flame, as shown in Fig. 7a, this line is observed very readily for 50 ppm solutions of magnesium against the very low OH background. In a normal air–acetylene or oxy-acetylene flame bismuth cannot be determined even in concentrated solutions by its emission at 3068 Å, and is only detectable at concentrations of *ca.* 1000 ppm, owing to interference from the OH band system which has a head at 3064 Å. Figure 7b shows the emission spectrum obtained for an 800 ppm solution of bismuth in the enriched separated air–acetylene flame. It is evident from this spectrum that bismuth may be determined with good precision in the range 100–1000 ppm and detected above the low background at concentrations as low as 40 ppm.

DISCUSSION

The flame separator provides a simple "closed" burner system, which is advantageous in shielding the flame from contamination by atmospheric dust, draughts and pressure variations. Separation of the air–acetylene flame practically eliminates the flame radiative background, and although the atomic line emission of elements introduced into the flame is also decreased slightly, the ratio of the intensity of the analytical emission signal to that of the flame background radiation is greatly increased for a given slit width. On the basis on which it is normally assessed this does not, however, give great advantage in the limit of detection for the elements investigated.

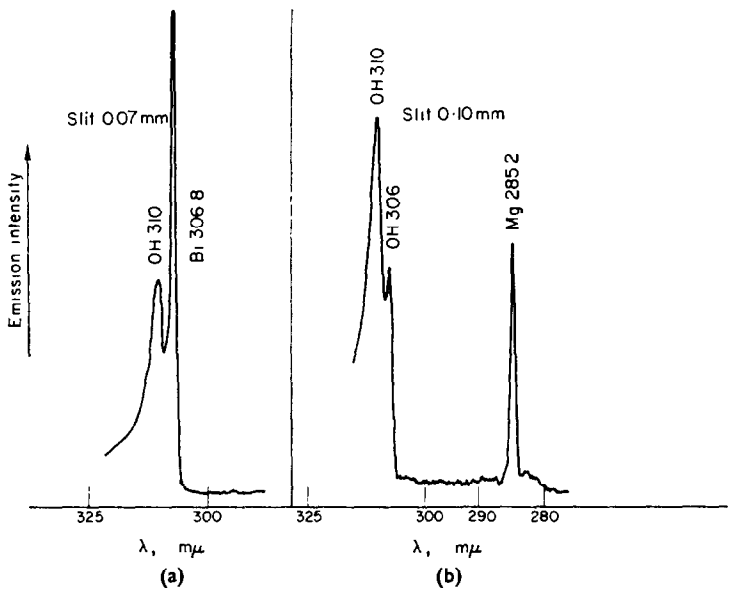

FIG. 7.—Part of the emission spectrum for (*a*) bismuth, 800 ppm, and (*b*) magnesium, 50 ppm, in the separated flame.

The reason for this is that normally in flame emission the limit of detection is defined as by the signal:background ratio. With the separated flame, however, where the radiative background has been very considerably reduced, the detection limit depends more on the signal:electrical noise ratio, as pointed out by Alkemade.[3] Consequently further improvement in limits of detection should be obtainable only by refinement of the detection and amplification system.

Oxygen enrichment of the air used for aspiration provides a separated air–acetylene flame of great utility, particularly for the emission photometry of elements which are difficult to excite. It is normally very difficult in unseparated flames to identify with certainty elements present at low concentrations in a sample simply by recording the emission spectrum of the flame and sample. It is usual under such circumstances to record the emission spectrum from the sample to which a high concentration of the suspected elements has been added. Positive identification of the elements in the original sample is then made from the small differences in the background spectrum with and without the sample at the wavelengths at which high concentrations were identified. The low emission background from the oxygen-enriched separated air–acetylene flame makes it possible to make qualitative assignments for elements

directly from flame emission spectra even for solutions of low concentration. The identification of Bi at 3068 Å and Mg at 2852 Å in this flame demonstrates this advantage.

The almost complete suppression of the OH emission band is a characteristic of the separated flame which cannot be fully taken advantage of in thermal emission flame photometry of the elements, owing to the high excitation energy requirements and consequent poor sensitivity of thermal emission methods in the OH band region between *ca.* 2800 and 3150 Å. Considerations of the background emission and excitation energy requirements lead us to believe that separated flames might prove more useful in atomic absorption and atomic fluorescence spectroscopy than in thermal emission spectroscopy. Our preliminary results for the use of separated flames in these techniques are very promising, and will form the subject of a later publication.

Acknowledgements—One of us (A.S.) is grateful to the University of Oslo, Norway for granting study leave. We also wish to thank Unicam Instruments Ltd. for the loan of the SP 900A flame spectrophotometer with which this work was carried out, and Murex Ltd. for the loan of the Sargent recorder.

Zusammenfassung—Die Auftrennung einer vorgemischten Luft-Acetylen-Flamme wird beschrieben. Die Zone zwischen den Kegeln dieser Flamme zeigt sehr geringen Strahlungsuntergrund und ist nur wenig kälter als die einer normalen Luft-Acetylen-Flamme. Der Gebrauch der aufgetrennten Flamme bei der Flammenphotometrie wurde untersucht; sie zeigt dabei mehrere deutliche Vorteile.

Résumé—On décrit la séparation d'une flamme air-acétylène préalablement mélangés. La zone inter-conique de cette flamme montre un très faible fond radiatif, et n'est que légèrement plus froide que celle d'une flamme air-acétylène normale. On a étudié l'emploi de la flamme séparée en photométrie de flamme, où elle offre plusieurs avantages prononcés.

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PRECIPITATION OF NICKEL DIMETHYLGLYOXIMATE

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Summary—The homogeneous precipitation method of Salesin and Gordon and the aqueous acetone precipitation described by Jones and Howick are examined for the determination of nickel as the dimethylglyoximate and where applicable comparisons are made with a direct (conventional) precipitation of this substance. The co-precipitation of iron and cobalt was studied radiometrically under various experimental conditions. Relevant solubility data are also presented. Application of the methods to the determination of nickel in alloy steels showed that in the absence of cobalt there is little to choose between them. For cobalt steels the method of Jones and Howick is more convenient than that of Salesin and Gordon and more satisfactory than a conventional precipitation and gravimetric finish.

SINCE the discovery[1] that dimethylglyoxime reacted with nickel(II) to give a highly coloured insoluble substance afterwards shown[2] to be suitable for the gravimetric determination of nickel, several refinements of the method and information on the structure of the substance have been reported.[3–7] The introduction of a method of homogeneous precipitation by Salesin and Gordon[8] (S & G) and the mixed solvent method of Jones and Howick[9] (J & H) are representative of more recent attempts to improve the selectivity of the method.

In the work described here these new quantitative methods are compared with a "conventional" precipitation method. Their application to the determination of nickel in some alloys has been examined and aspects of the coprecipitation of cobalt and iron studied by using radioactive tracers. As part of this study the solubility of nickel dimethylglyoximate in various solvent media has been determined radiometrically.

EXPERIMENTAL

Reagents and apparatus

Reagent-grade chemicals were used unless otherwise stated.

Nickel. An aqueous solution containing about 3 mg of nickel per ml was prepared from nickel sulphate heptahydrate. The nickel content was determined by dimethylglyoxime precipitation.[10]

Cobalt and iron. Aqueous solutions, each containing about 2 mg of metal ion per ml, were prepared from hydrated cobalt(II) and iron(III) chlorides and standardized by EDTA titration.[11,12]

Radioactive tracer solutions. The radioactive isotopes cobalt-60, nickel-63 and iron-59 were obtained from the Radiochemical Centre, Amersham, England. Each contained some carrier. The stock solutions were diluted to the required activity levels with 1*M* hydrochloric acid.

Biacetyl. Laboratory reagent grade biacetyl (B.D.H., Poole, England) was redistilled before use as recommended by Salesin and Gordon.[8] The refractive index (1·394) measured by means of an Abbé refractometer, was used as a measure of purity.

Dimethylglyoxime. A 1% w/v solution was prepared in ethanol.

Sodium diethyldithiocarbamate. A 2% w/v aqueous solution was freshly prepared each day.

Scintillator. The initial experiments were carried out with a solution containing 0·5 g of 2,5-diphenyloxazole (PPO) and 0·05 g of 1,4-bis[2-(5-phenyloxazolyl)]benzene (POPOP) dissolved in 1 l. of toluene. Later, it was found that the commercially available scintillator NE 214 [Nuclear Enterprises (G.B.) Ltd., Edinburgh, Scotland] was more satisfactory and it was used in the work reported here.

Buffer, pH 6·4. An ammonium acetate–acetic acid solution, 5*M* in acetate, was used.

Hydroxylamine hydrochloride. A 1·8% w/v aqueous solution was used.

Alloys. The analysed alloy samples were British Chemical Standards (B.C.S.) supplied by the Bureau of Analysed Samples Ltd., Middlesbrough, England.

Radioactive counting

The cobalt-60 and iron-59 were counted in a well-type γ-scintillation counter [Na(Tl)I crystal] by using the photopeaks produced by the 1·17 and 1·33 MeV γ-rays from the cobalt and the 1·29 MeV ray from the iron.

Nickel-63 was determined by a liquid scintillation counting method. The apparatus consisted of a single photomultiplier tube (EMI 6097S type) having a satisfactory signal/noise response, used in conjunction with pre- and main amplifiers (NE 5202) and suitable discriminating equipment (single channel pulse height selector NE 5102) all supplied by Nuclear Enterprises (G.B.) Ltd.

Precipitation of nickel

Portions (10 ml) of the standard nickel solution were measured out by pipette and the procedures set out by Gordon *et al.*,[8,13,14] Jones and Howick[9] and, for example, Vogel[10] for the direct precipitation method, were followed.

Coprecipitation of cobalt and iron

The method used was similar to that described previously[15] for a study of the coprecipitation of various metal ions with aluminium tris-8-hydroxyquinolinate. The final volume of solution from which precipitation occurred was, however, 200 ml, and the weighed portion of precipitate was dissolved in a mixture of 10 ml of 1*M* sulphuric acid and enough acetone to make the final volume 25 ml. Portions (5 ml) of this solution were counted.

The measure of the total tracer activity present was obtained by diluting 2 ml of the tracer and 10 ml of the carrier nickel solutions to 100 ml with sulphuric acid and acetone in the proportions used for dissolving the precipitate, and counting 5 ml of the solution. Varying amounts of inactive nickel or dimethylglyoxime within the required range did not influence the counting efficiency for the two isotopes used.

The proportion of tracer, W%, coprecipitated with the nickel was calculated from the relation

$$W = \frac{x}{4yz} \times 100$$

where y is the initial and x the final counting rate; z is the fraction (by weight) of the precipitate dissolved in the step leading to x.

Solubility of nickel dimethylglyoximate

Samples of nickel dimethylglyoximate containing nickel-63 were carefully prepared by precipitation from dilute nickel solutions. Excess of the dried substance was shaken mechanically for 24 hr with the chosen solvent at room temperature (23°). The equilibrated mixtures were filtered through a sintered glass crucible (porosity No. 4) or through a Whatman No. 41 filter paper. Then 100 ml of the filtrate were pipetted into a 400-ml tall-form beaker and the contents carefully evaporated to near dryness after the addition of 1 ml of concentrated hydrochloric acid. The nickel was transferred to a separating funnel by rinsing the beaker with successive 2–3 ml portions of water each containing a drop of concentrated hydrochloric acid. Ten ml of buffer at pH 6·4 and 10 drops of diethyldithiocarbamate solution were added and the nickel was extracted into 10 ml of toluene. Two ml of the toluene phase were mixed with 5 ml of scintillator solution and counted. Colour quenching of the scintillator was found to be negligible if less than about 6 μg of nickel were present during counting of the sample; for larger amounts of nickel counted a correction was applied by using a calibration curve. The specific activity of the nickel dimethylglyoximate was determined by dissolving a weighed portion in 3 or 4 drops of hydrochloric acid, adding 10 ml of buffer at pH 6·4 and extracting the nickel into toluene as just described. Experiments showed that for the amounts of nickel involved, the single extraction of the carbamate proved adequate. The extractions from tartrate media were carried out directly on the equilibrated solutions without evaporation.

Nickel in alloy steels

Sufficient of the sample was weighed to contain 25–35 mg of nickel. It was dissolved in 15 ml of 8*M* nitric acid and 5 ml of concentrated hydrochloric acid and oxides of nitrogen were expelled. The solution was diluted to about 180 ml and an amount of tartaric acid equal to 8 times the sample

weight was added; any solid remaining was filtered off and the pH of the solution adjusted with concentrated aqueous ammonia to 7·5 for precipitation by the S & G method or 8 to 8·5 for the J & H method. In the latter method, 75 ml of acetone were added followed by the dimethylglyoxime. For a 1-g alloy sample, the acetone/water ratio should not exceed 1/3 v/v. The determinations in both cases were completed according to the instructions of the respective authors.[8,9]

For alloys containing appreciable amounts of cobalt, 1 g of sodium sulphite was added in the S & G method to ensure that cobalt(II) only was present during the precipitation. In order to obtain complete precipitation in cobalt alloys it was necessary, as pointed out in the original paper,[8] to set the solution aside for at least 24 hr before heating or to add some dimethylglyoxime at the end to ensure complete precipitation of nickel.[8] In the J & H method, the dimethylglyoxime should be added slowly to the hot solution (60–70°) when cobalt is present.

Precipitates are collected from cooled solutions to reduce the solubility of the nickel dimethylglyoximate.[4]

RESULTS AND DISCUSSION

Batches of 10 determinations were carried out for each of the three methods of analysis, on portions of the same nickel solution. The mean precipitate weights obtained are presented along with calculated standard deviations in Table I. It was found that unless the biacetyl was sufficiently pure, high results were obtained by the

TABLE I.—SUMMARY OF RESULTS ON THE PRECIPITATION OF NICKEL

Method	Salesin & Gordon	Jones & Howick	"Conventional"
Precipitate weights, *g*	0·1488	0·1489	0·1492
Standard deviations, *g*	0·0001	0·0001	0·0003

S & G method. For example, biacetyl used directly from the bottle and having a refractive index of 1·4220 gave 0·1504 ± 0·0001 g (10 measurements) for the same quantity of nickel as that used to obtain values recorded in Table I. Additional experimentation with nickel-63 tracer showed that the difference in weight was not due to a more efficient precipitation of the nickel. It was also found that the impurity could not be removed by prolonged drying of the precipitate at 140°.

Some coprecipitation studies were carried out to examine the efficiency with which the S & G and J & H methods prevent entrainment of cobalt and iron. The J & H method gives rapid precipitation following addition of the dimethylglyoxime; a study of coprecipitation with fractional precipitation of the carrier was not possible and measurements are therefore limited to conditions giving complete precipitation of the nickel. A more extensive study proved possible with the S & G method and the results are reported in Figs. 1 and 2. Tables II and III give coprecipitation data for both methods when precipitation of the carrier is 100%.

The results in Fig. 1 show that for tracer and mg quantities of cobalt(II) coprecipitation is quite low, increasing linearly with increase in the fraction of carrier precipitated. For tracer and 1 mg quantities of cobalt(II) the fraction entrained in the precipitate is higher than for larger concentrations, for which coprecipitation increases roughly proportionally to the amount (and hence concentration) present initially. Extrapolation backwards would suggest that the curves (Fig. 1) pass through or close to the origin, indicating that cobalt does not give rise to centres (nuclei) from which crystals grow. The presence of small amounts of silica does not have any effect on the coprecipitation of tracer amounts of cobalt(II) (Fig. 2) thus supporting this conclusion. Coprecipitation appears to be a little higher when the precipitation of

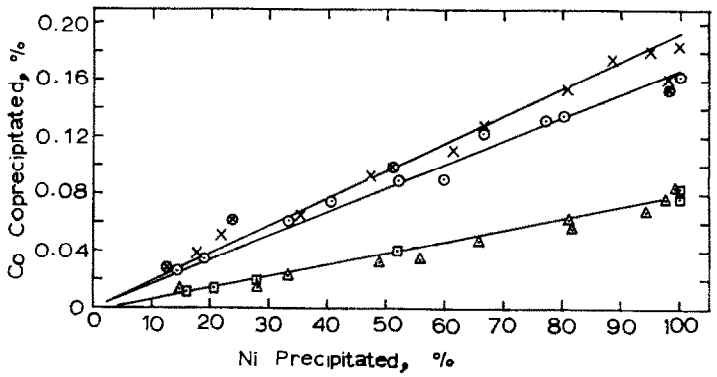

FIG. 1.—The coprecipitation of cobalt(II) with nickel dimethylglyoximate precipitated at 50°C.
×—6×10^{-5} mg of Co; ○—1·05 mg of Co; △—10·5 mg of Co; ⊡—31·5 mg of Co present; all data refer to unstirred solutions: ⊗—6×10^{-5} mg Co in a continuously stirred system.

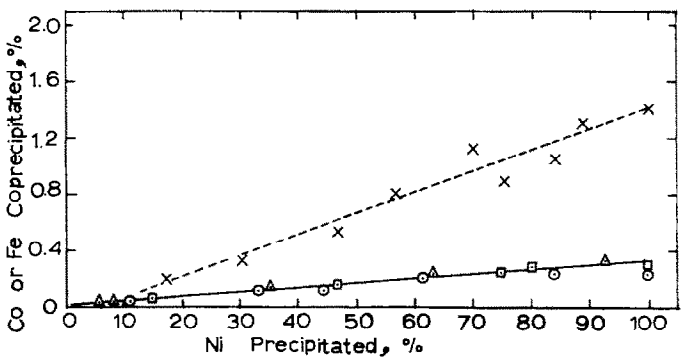

FIG. 2.—The coprecipitation of cobalt(II) and iron with nickel dimethylglyoximate at 23°.
×—4×10^{-5} mg of Fe; △—6×10^{-5} mg of Co; pH 6·8–7·0; ⊡—6×10^{-5} mg Co + silica gel (2·5 mg); ⊙—6×10^{-5} mg Co present: all data refer to unstirred solutions.

nickel is carried out at room temperature (Fig. 2) rather than at 50° (Fig. 1). The rate of precipitation is higher at the higher temperature; qualitatively the observed trend is therefore in agreement with that found by Schweitzer and McDowell[16] when studying the coprecipitation of cobalt with nickel precipitated conventionally. The results presented in Figs. 1 and 2 were mainly obtained with unstirred solutions; continuous stirring produced precipitates having an almost gelatinous character, but when tracer cobalt was present, coprecipitation did not show a significant change (Fig. 1).

Where comparison is possible between the coprecipitation data of Schweitzer and McDowell and that of Table II, cobalt entrainment is appreciably less by the homogeneous precipitation method. Increase in digestion time increased coprecipitation in the earlier, but not in the present work.

Results are given in Fig. 2 for the coprecipitation of tracer iron with fractional precipitation of nickel at room temperature by the S & G method. For complete

TABLE II.—COPRECIPITATION OF COBALT FOR COMPLETE PRECIPITATION OF NICKEL

Exp.	Method	Total cobalt present, *mg*	Temp. of precipitation, °C	Cobalt coprecipitated as % of total Co
1	S & G	T	50	0·17
2	S & G	T	23	0·24
3	S & G	1·05	50	0·16
4	S & G	10·5	50	0·85
5	S & G	31·5	50	2·48
6	S & G	1·05	50	0·17
7	S & G	1·05	23	0·50
8	S & G	T	23	0·08
9	S & G	1·05	23	0·10
10	J & H	T	70	$<2 \times 10^{-3}$
11	J & H	10·5	70	$<2 \times 10^{-3}$

In experiments 6 and 7 the solution contained 60·52 mg of Ni, in the others 30·26 mg. An addition of 1 g of tartaric acid +1 g of sodium sulphite was made before precipitation in 8 and 9. T means that only tracers of cobalt (approx 6×10^{-5} mg) were added. The values in column 5 are means of duplicate determinations.

TABLE III.—COPRECIPITATION OF IRON FOR COMPLETE PRECIPITATION OF NICKEL

Method	Iron present, *mg*	Temp. of precipitation, °C	Iron coprecipitated as % of total Fe	Additions
S & G	T	23	0·15	—
S & G	T	23	0·17	+1 g Na_2SO_3
S & G	T	23	<0·005	+1 g tartaric acid
S & G	25	23	<0·005	+1 g tartaric acid
S & G	25	23	<0·005	1g Na_2SO_3 + 1g tartaric acid
J & H	T	70	<0·005	—
J & H	30	70	<0·005	—
J & H	60	70	<0·005	—

In each experiment 30·26 mg of nickel were precipitated. T indicates that only traces of iron (approx 4×10^{-5} mg) were added. Column 5 gives additions over and above those mentioned in the basic procedure. Measurements were performed in duplicate.

precipitation of nickel the extent of iron coprecipitation is summarized in Table III under various reaction conditions. Thus, in the presence of tartaric acid, iron in moderate amounts should not present a problem through coprecipitation in either method (see also Table VII). The presence of sodium sulphite does not have a significant effect on iron entrainment.

Solubility studies

The results of measurements of the solubility of nickel dimethylglyoximate in various fluid media are given in Table IV. Good agreement is found where comparison with published data is possible. The solubility is lowest in water. The substance is less soluble in ethanol or ethanol/water than in acetone or acetone/water. Moderate

TABLE IV.—SOLUBILITY DATA AT 23° FOR NICKEL DIMETHYLGLYOXIMATE

Solvent	No. of measurements	Mean solubility (g $NiDMG_2$/100 ml)
Water (pH 6·9–7·0)	3	$(3{\cdot}4 \pm 0{\cdot}3) \times 10^{-5}$
2% w/v Ammonium acetate	3	$(1{\cdot}3 \pm 0{\cdot}1) \times 10^{-4}$
1:1 v/v Acetone/water	2	$2{\cdot}7 \times 10^{-4}$
1:1 v/v Ethanol/water	2	$1{\cdot}9 \times 10^{-4}$
Acetone	2	$3{\cdot}8 \times 10^{-4}$
Ethanol	4	$(1{\cdot}4 \pm 0{\cdot}1) \times 10^{-4}$
1·5% w/v Ammonium tartrate pH 7·5	2	$1{\cdot}4 \times 10^{-4}$
4% w/v Ammonium tartarate pH 7·5	2	2×10^{-4}

Published data: in water at 25°, $3{\cdot}6 \times 10^{-5}$ g $NiDMG_2$/100 ml:[17] in 1:1 ethanol/water at 25°, $2{\cdot}4 \times 10^{-4}$ g Ni DMG_2/100 ml.[4]

concentrations of ammonium acetate or tartrate appear only to have a small effect. It is therefore to be expected that the loss of nickel in terms of the weight of dimethylglyoximate (0·1 or 0·2 mg) may be just measurable in the usual gravimetric determination. This conclusion finds support from results obtained for some experiments in which nickel labelled with nickel-63 was precipitated by the two methods under consideration (see Table V). The amount of nickel left in solution (Table V) is in

TABLE V.—LOSSES IN THE PRECIPITATION OF NICKEL

Method	Ni taken, *mg*	Vol. of soln, *ml*	Ni left in soln, *mg*/100 *ml*
S & G	30·26	200	0·020
			0·016
J & H	30·26	160	0·024
			0·035

reasonable agreement with that found by Salesin and Gordon[8] who also included precipitate washings (not so here) in their measurement. The loss per unit volume by the J & H method is somewhat greater possibly due to residual acetone and ammonia at the higher pH used. Results in Table IV suggest that the frequent text-book statement on the need to keep the ethanolic content of the mother liquor minimal is not explained (if justified) in terms of solubility of the precipitate.

Small concentrations of ammonium acetate should not contribute greatly to loss of nickel in a precipitation. On the other hand, free ammonia is probably best kept at a minimum. Experiments showed that the red nickel precipitate dissolves appreciably. For example, 100 ml of ammonia solution (1 + 1) take up about 37 mg of the red solid to give a clear solution. When the ammonia was expelled by boiling the original amount of red precipitate reappeared. It is therefore unlikely that appreciable nickel is converted by aerial oxidation into nickel(IV) under strongly ammoniacal conditions as has been suggested by Claassen and Bastings.[5]

Alloys

Table VI gives results for the analysis of various alloy steels. The agreement between the values given by the S & G and J & H methods and the mean values obtained from the control laboratories is good. Table VII summarizes data from experiments carried out to check that the results in Table VI were not due to compensatory effects. They were obtained by adding iron-59 or cobalt-60 to the alloy sample at

TABLE VI.—NICKEL IN ALLOY STEELS

B.C.S. No.	Nickel found, %		Nickel, %	Reported alloy contents Main constituents
	S & G method	J & H method		
254/1	3·25	3·25	3·26	Low alloy steel. Fe, ~95%
	3·25	3·25		
	3·25	3·24		
235/2	9·38	9·38	9·38	Ti-stabilized '18–9' stainless steel.
	9·38	9·38		
	9·40	9·39		
261	13·09	13·09	13·08	Nb-stabilized '18–12' stainless steel.
	13·09	13·08		
	13·08	13·09		
219/3	2·53	2·53	2·52	Ni–Cr–Mo steel. Cr, 0·76%; Mo, 0·60%.
	2·52	2·52		
	2·52	2·53		
233	11·25	11·22	11·22	Permanent magnet alloy. Co, 23·72%; Cu, 5·09%; Al, 6·98%.
	11·24	11·23		
	11·24	11·23		
312	13·7	13·6	13·6	Permanent magnet alloy. Co, 23·6%; Cu, 3·10%; Nb, 1·33%; Ti, 1·19%; Si, 1·13%.
	13·8	13·7		
	13·8	13·8		

its dissolution. For alloys in which cobalt is absent the conventional method of direct precipitation also gave good results; in the presence of cobalt, the method without modification is unsatisfactory.[5] In the absence of cobalt the S & G, the J & H and the conventional methods take about 6, 5 and 4 hr respectively for a single determination. There is thus little advantage in using the longer methods other than the possible one that either of them could be used more reliably by less experienced operators than the direct precipitation method.

TABLE VII.—CONTAMINATION OF THE NICKEL DIMETHYLGLYOXIMATE FROM ALLOY STEELS

Alloy	Approx weight of alloy, *g*	Method of separation	Contamination *mg*	
			Iron	Cobalt
BCS254/1	1	S & G	<0·02	—
		J & H	<0·02	—
BCS261	0·2	S & G	<0·005	—
		J & H	<0·005	—
BCS233	0·2	S & G	0·12	0·006
		J & H	<0·01	<0·0005
BCS312	0·2	S & G	0·09	0·006
		J & H	<0·01	<0·0005

In the presence of cobalt the J & H method appears to be decidedly advantageous in that cobalt contamination of the nickel dimethylglyoximate is not significant and the analysis only takes about 5 hr compared to 24 by the S & G method. Collection of the precipitate is facilitated by the absence of "creeping" and adsorption on the beaker walls.

Zusammenfassung—Die homogene Fällungsmethode von Salesin und Gordon und die von Jones und Howick beschriebene Fällung aus wäßrigem Aceton werden zur Bestimmung von Nickel als Dimethylglyoximat überprüft und nach Moglichkeit mit einer direkten (herkömmlichen) Fällung dieser Substanz verglichen. Die Mitfällung von Eisen und Kobalt wurde radiometrisch unter verschiedenen experimentellen Bedingungen untersucht. Wesentliche Löslichkeitsdaten werden ebenfalls mitgeteilt. Die Anwendung der Methoden auf die Bestimmung von Nickel in legierten Stählen zeigte, daß sie in Abwesenheit von Kobalt praktisch gleichwertig sind. Bei Kobaltstählen ist die Vorschrift von Jones und Howick bequemer als die von Salesin und Gordon und besser als eine herkommliche Vorschrift mit gravimetrischem Abschluß.

Résumé—La méthode de précipitation homogène de Salesin et Gordon et la précipitation à l'acétone aqueuse décrite par Jones et Howick sont examinées pour le dosage du nickel à l'état de diméthylglyoximate et, là où la chose est applicable, on effectue des comparaisons avec une précipitation directe (ordinaire) de cette substance. On a étudié la coprécipitation du fer et du cobalt par radiométrie sous diverses conditions expérimentales. On présente aussi des données de solubilité s'y rapportant. L'application des méthodes au dosage du nickel dans les alliages d'acier a montré qu'en l'absence de cobalt il y a peu de choses permettant de choisir entre elles. Pour les aciers au cobalt, la méthode de Jones et Howick est plus commode que celle de Salesin et Gordon et plus satisfaisante qu'une précipitation ordinaire et une fin gravimétrique.

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A HIGH SPEED MICRO VACUUM-FUSION APPARATUS

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Summary—A micro vacuum-fusion apparatus capable of extracting, collecting and examining volumes of gas of no more than 2×10^{-3} cm³ at N.T.P. from metal samples is described. The resulting gas mixture is analysed by gas chromatography with helium as the carrier gas and with a highly sensitive ionization detector.

THE importance of trace impurities in metals, alloys and semiconductors needs no emphasis. Among the most difficult elements to remove from these materials are the permanent gases, since they are present in measurable quantities even in moderately good vacuum systems. Analysis for the permanent gases is therefore of considerable importance. Gas analysis has been applied to progressively smaller samples with a decreasing gas content (<10 ppm) and to a wider range of materials, with only partial success. For example, the determination of nitrogen in the refractory metals is not certain.[1] Thermodynamic data available lead one to the conclusion that nitrogen should be completely extracted from these metals when they are melted in an iron or platinum bath during a vacuum fusion experiment. There is, however, some factor as yet not determined which prevents the rapid removal of nitrogen. Furthermore, with smaller total amounts of gas to be extracted, the apparatus blank and its composition become of extreme importance. Almost certainly a compromise has to be made between the time taken for gas extraction and the fraction of the gas collected that is due to the apparatus blank. A further compromise has to be made between the temperature at which extraction takes place and the amount of material that can be evaporated from the bath. Such material, particularly the refractory metals and manganese, can act as "getters" and thus may remove the extracted gases from the system before they can be collected. Ideally, therefore, gas extraction should be carried out as rapidly as possible at a temperature just high enough for the gases to be extracted quickly. If, in addition, one of the constituents of the bath is volatile then it should be present as only a small fraction of the bath material so as to reduce its vapour pressure.

The purpose of this paper is to describe a micro vacuum-fusion apparatus to which has been coupled a recently developed gas chromatographic analytical system. Emphasis has beeen laid on simplicity of apparatus, speed of extraction and low blank together with good gas extraction and collection conditions.

EXPERIMENTAL

Apparatus

Furnace. The furnace-head is made of silica and is cooled by a jet of air (Fig. 1). A 2-mm diameter tungsten rod supports the graphite crucible assembly. The graphite that has been used is type EY9A, manufactured by the Morgan Crucible Co. Ltd. The crucible is supported in an outer graphite thimble, wall thickness 2 mm, by a layer of loosely packed 300-mesh graphite powder about 3 mm thick. The powder serves to curtail excessive radiation from the crucible when it is at its working

or outgassing temperature, and to insulate the crucible electrically from the thimble. A medium frequency (5000 c/s) generator supplies the power to the heating coil. The inner crucible is preferentially heated because of the wall thicknesses chosen. The central cavity in the crucible is 1 cm in diameter and 4 cm long, so giving a working volume of 3 cm^3, and the wall thickness is greater than 1 cm. A graphite ball is used as a lid to the crucible.

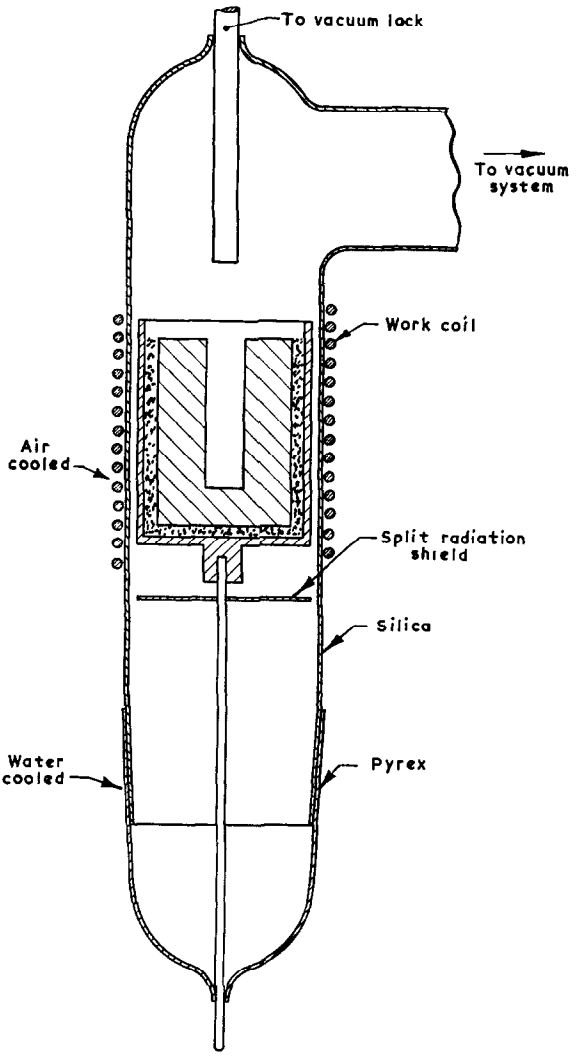

FIG. 1.—The graphite crucible assembly.

In addition to heating the crucible the use of a low frequency power supply results in efficient stirring of the melt. This method ensures that a large effective surface area is presented to the vacuum as compared with the languid conditions in a melt stirred only by convection currents, which is the case when radio-frequency (*e.g.*, 400 kc/s) heating is used. This is considered by Sloman[2] to be a major factor leading to the rapid and complete extraction of gases from such melts. Theoretically it is only necessary for the partial pressure of a gas in the melt to be greater than that in the space above, and if this condition is fulfilled the extraction rate depends on the time of exposure of the gas at the melt surface to the pumped void. Thus with other things being equal, the gas will be extracted at a rate proportional to the surface area.

Vacuum system. The furnace is pumped out by a conventional vacuum system using two high-speed mercury diffusion pumps in series. The gas evolved from the specimens is trapped in the pumping line between these pumps by closing tap T_1 shown in Fig. 2. Mercury diffusion pumps have been chosen for two reasons. First, the pumping "head" of these pumps is such that a large quantity of gas can be collected in the manner described without the pumping action being stopped. Secondly, as the pumps are used without traps in order to simplify the apparatus and to maintain high pumping speeds, some back-streaming of the pumping fluid must occur but it is not important in the case of mercury.

Samples to be analysed are held in a tube above the furnace ready to be dropped vertically through a high-vacuum stop-cock into the crucible. This tube, closed to the atmosphere by a stainless steel cap, constitutes with the stop-cock a simple vacuum lock. A guide is placed so as to keep the samples to the middle of the tube during the drop, to prevent contamination from the grease of the stop-cock.

Gas analysis. The extracted gas is analysed by the chromatographic method described previously;[8] briefly, this consists of an analytical column packed with molecular sieve powder. A Lovelock

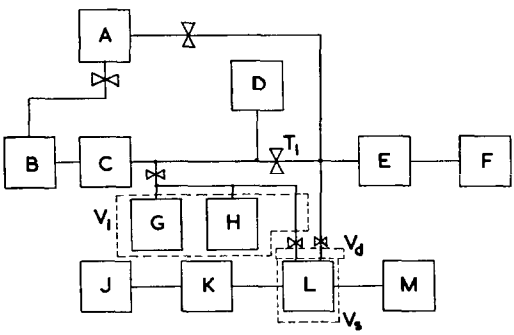

FIG. 2.—Schematic diagram of the vacuum system and gas chromatograph.
A, vacuum lock; *B*, furnace; *C*, first diffusion pump; *D*, Pirani gauge; *E*, second diffusion pump; *F*, rotary pump; G, molecular sieve trap; *H*, adjustable volume; *J*, helium cylinder; *K*, helium purifier; *L*, sample loop; *M*, gas chromatograph. V_1, V_d and V_s are referred to in the text.

ionization detector is used which requires helium carrier gas. The analytical column, 120 cm long and 0·5 cm in diameter, is packed with Linde 5A molecular sieve powder, 36–60 mesh. The fines are removed by washing the powder in a tall beaker with a jet of water at such a flow-rate that the fine particles are washed out of the beaker while the coarser ones sink back towards the jet. It has been found that packing material treated in this manner gives sharp elution peaks. Retention times for various gases are given in Table I. The column is heated to 125° in order to elute carbon monoxide

TABLE I.—RETENTION TIME FOR VARIOUS GASES

Gas	Retention time, *sec*
Hydrogen	32
Oxygen	50
Argon	49
Nitrogen	64
Methane	90
Krypton	105
Carbon monoxide	150

reasonably quickly. At this temperature the nitrogen and oxygen peaks are well resolved. If determination of oxygen in the gas mixture is not required the analytical column can be run at a temperature high enough just to resolve the hydrogen and nitrogen peaks. The retention time of carbon monoxide will then be less and the analysis time shorter.

A "Loenco" 6-way valve, supplied in Britian by D. Pitman and Co., Weybridge, Surrey, is used to inject a sample of the gas mixture into the carrier stream. The sampling loop of the valve has a volume of 1 cm^3 and the sample gas pressure used had a maximum of 1 torr, *i.e.*, a maximum quantity of gas mixture of about $1{\cdot}3 \times 10^{-3}$ cm^3 at N.T.P. could be injected. With a carrier gas flow-rate of 90 cm^3/min and a detector voltage of 220 V this quantity of pure gas gives a peak current of 10^{-8} A, corresponding to near minimum amplifier sensitivity settings.

Gas handling apparatus. The extracted gases trapped in the pumping line to the diffusion pump occupy a large volume at low pressure. To obtain good injection conditions for the gas chromatograph this gas has first to be compressed into a small volume at a relatively high pressure. This is accomplished by pumping the trapped gas on to Linde 5A molecular sieve pellets held in a volume of 2 cm^3 and chilled by liquid nitrogen. After this pumping is complete and the 2-cm^3 volume isolated, the gases are quantitatively released by heating the trap to 200° for 3 min. The times taken to absorb (at −196°) and release the gases (at 200°) are given in Table II. The gas mixture is then expanded into the evacuated sample loop of the sampling valve. The volume of the associated dead space is 1 cm^3.

TABLE II.—TIME OF ABSORPTION AND DESORPTION FOR VARIOUS GASES

Gas	Time, *sec*	
	Absorption	Desorption
Hydrogen	180	5
Nitrogen	30	40
Methane	40	60
Carbon monoxide	5	150

The gas chromatograph can accept a pressure in the sample loop in the range 0·05–2·0 torr, depending on the composition of the mixture, without overloading the detector. Provision is therefore made to keep the pressure within this range by having a calibrated tube, which can be filled with mercury, on a side-arm to the trapping volume. By adjustment of the mercury level in this tube any known volume up to 12 cm^3 can be added when necessary. This facility is also necessary to enable the trapping volume, V_1, the dead space, V_d, and the volume of the sample loop, V_s, to be found quite easily by a gas expansion method (see Fig. 2). A mercury manometer is added to the trapping volume for this purpose.

RESULTS

To reach the outgassing temperature of 2400° an indicated power of 12 kW is required but 7 kW will enable 1600° to be reached. With the inner crucible at 2400° the outer thimble attains a temperature of 1000°. With new graphite in the crucible assembly an outgassing time of 6 hr is necessary but once the graphite has been outgassed, subsequent outgassing procedures require only 1½–2 hr. The blank rate desired is such that the contribution of the blank to the total volume of gas collected is less than 10%, *i.e.*, about 1×10^{-3} cm^3/hr at N.T.P. Generally, the blank rate rises to this value after the bath material is added to the crucible. A typical blank analysis before the bath material is added is 83% H_2, 4% CH_4 and 13% CO. After the bath material has been added the figure for hydrogen increases slighly. There is never more than a trace of nitrogen unless there is a vacuum leak. It is interesting that, although the analytical system has sufficient sensitivity, oxygen is not always found when there is a leak, probably because of a reaction between oxygen and the hot graphite of the furnace.

Gas extraction from pure iron and chromium specimens appears to be complete after 3 min. None of these specimens contained more than a total of 20 ppm of gaseous impurities. The gas extraction process is monitored by the Pirani gauge (Fig. 2). Pressure changes rather than absolute readings are noted since the sensitivity of the gauge varies with gas composition. Use is made of the maximum reading to calculate

any volume adjustment required to the molecular-sieve trap as described in the previous section. When once this volume has been fixed for a particular sample the gases are pumped into the molecular-sieve trap during extraction to minimize the effect of the apparatus blank. It is possible to complete the extraction and analyse the resultant mixture in 8 min.

Figure 3 shows the concentrations of oxygen, nitrogen and hydrogen found at different points along a 2·5 mm diameter iron rod which had been subjected to floating-zone levelling and should have been of constant composition throughout. The specimens, numbered in order from 1 to 9 along the rod were analysed in the sequence 1, 6, 2, 7, 3, 8, 4, 9, 5. Apart from specimens 5, 6 and 7 the values found were oxygen 7 ppm, nitrogen 0·5 ppm and hydrogen 1·7 ppm. Thus with a sample expected to be uniform, reasonably constant results were obtained. The reason for the high values obtained for specimens 5, 6 and 7 is not known but it is not a function of the apparatus nor of the extraction procedure. Possibly a region containing a substantial amount of oxygen and other foreign matter in the original material has not been degassed by the zone-levelling process but has been merely spread out. As is usual, the scatter among the oxygen results is larger than that for the other gases.

An analysis was made of electrolytically prepared chromium flake which had been heated in hydrogen at 1350° for 2 hr. Typical flakes were about 1 mm thick and weighed 0·5 g, and, for the purpose of analysis, were carefully broken into four equal portions. For any one flake the analysis was reasonably constant but from flake to flake the results varied markedly, particularly for oxygen. For example, the analysis of one flake was: hydrogen, 4,3, 3·5, 3·5 ppm, nitrogen, 7, 8, 8, 9 ppm and oxygen, 18, 15, 17, 17 ppm, and for another, 4, 3·5, 3·5, 3 ppm, 7, 8·5, 8, 8 ppm and 11, 10, 10, 10 ppm respectively. For comparison, specimens (up to 10g) of a representative portion of the sample were analysed by a larger apparatus and found to contain 5 ppm of hydrogen, 8 ppm of nitrogen and 22 ppm of oxygen. These results show the reproducibility of the apparatus and procedure when it can be expected that the gas content of the specimens is constant. Variation from flake to flake is therefore a gross segregation phenomenon.

Segregation can be clearly seen in Fig. 4, which gives the analysis for oxygen along a pure iron bar that had been rolled from a 25-kg ingot to 1 cm diameter and then swaged to 2·5 mm diameter. This was the starting material for the zone-levelling purification treatment mentioned previously. The weight of the specimens used for this experiment ranged from 0·05–0·15 g. The result found for an 18-g specimen of the same sample in a larger apparatus was 28 ppm compared with an average value of 32 ppm for the small samples, for which the standard deviation was 13 ppm.

CONCLUSIONS

The sensitive apparatus described in this paper has been used for the gas analysis of pure iron and chromium flake. The results have shown that gas segregation is present in all materials so far examined unless special treatments such as zone-levelling or vacuum annealing were used. Once the apparatus had been outgassed one specimen could be handled every 10 min. The vacuum lock enabled specimens to be analysed in any order, and because the lock is evacuated by a by-pass pumping line it should be possible to carry out special surface cleaning treatments, such as argon ion-bombardment, before analysis. Owing to the simplicity of the apparatus high pumping speeds

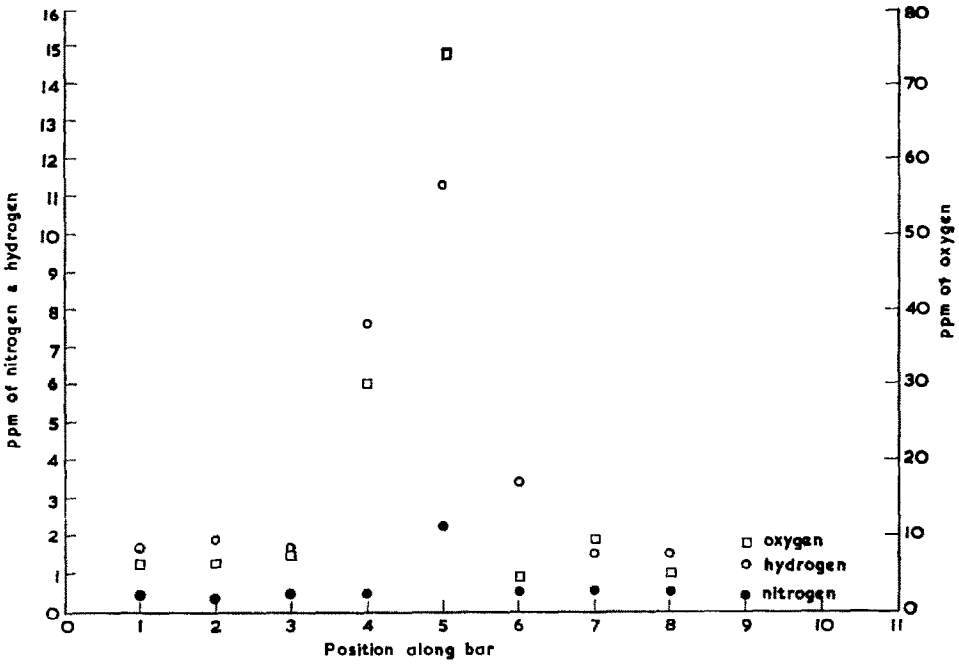

FIG. 3.—Distribution of oxygen, hydrogen and nitrogen along a zone-levelled iron bar.

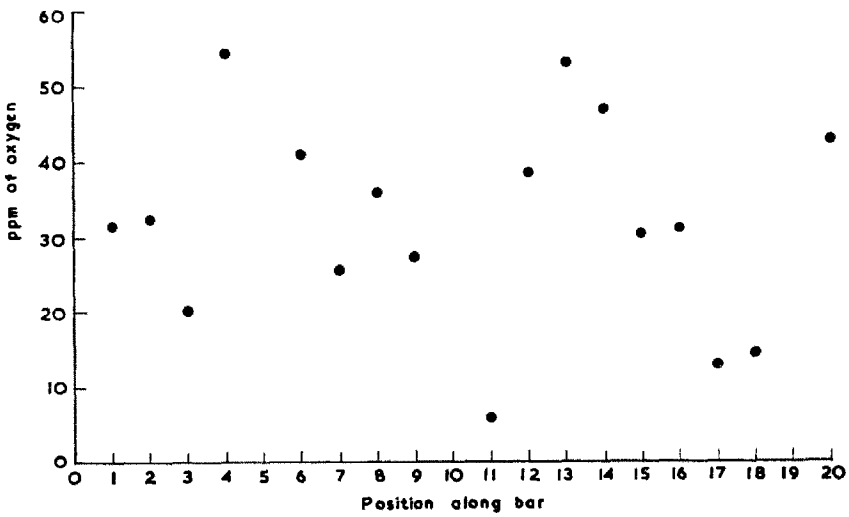

FIG. 4.—Distribution of oxygen along a swaged iron bar.

could be maintained and the extracted gas easily collected. The apparatus is of most use for samples having a very low gas content or for the study of gas segregation.

Acknowledgements—The author would like to thank Mr. I. M. Andrews who zone-levelled the pure iron used in some of the experiments and Mr. D. G. Gladman who helped in the construction of this apparatus.

Zusammenfassung—Eine Mikro-Vakuumschmelzapparatur wird beschrieben, mit der Gasvolumina von nicht mehr als $2 \cdot 10^{-3}$ cm³ bei Normalbedingungen aus Metallproben extrahiert, gesammelt und untersucht werden konnen. Das gewonnene Gasgemisch wird gaschromatographisch mit Helium als Trägergas und einem hochempfindlichen Ionisationsdetektor analysiert.

Résumé—On décrit un appareil de microfusion sous vide capable d'extraire, de recueillir et d'examiner des volumes de gaz n'excédant pas 2×10^{-3} cm³ à température et pression normales à partir d'échantillons de métaux. Le mélange gazeux résultant est analysé par chromatographie en phase vapeur avec l'hélium comme gaz porteur et avec un détecteur à ionisation hautement sensible.

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MASS SPECTROMETRIC ANALYSIS OF HIGH-PURITY HELIUM AND HYDROGEN, USING A DYNAMIC SAMPLING AND CALIBRATION SYSTEM

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Summary—A dynamic gas sampling system has been designed for use with a mass spectrometer (A.E.I. Model MS2G). It is capable of sampling directly from gas streams at pressures in the region of 800 torr and has been satisfactorily used for the analysis of high-purity helium and hydrogen containing less than 50 vpm total impurity. The overall sensitivity is 1 vpm or better. The design permits the mass spectrometer to be used with its normal gas sampling system when required. A dynamic gas blending rig, incorporating a recirculation and purification system, has been developed for the calibration of the mass spectrometer over the range 5–100 vpm of impurity content.

IN recent years a demand for high-purity gases such as helium has arisen, and in order to ensure that these gases comply with the relevant specifications analytical techniques of high sensitivity are required.

MS2G mass spectrometers (A.E.I. Ltd) are used for certain gas analyses in this Inspectorate, but in their normal configuration they are relatively insensitive *e.g.*, if the instrument is used normally, the limit of detection of an impurity in a gas is in the region of 50 vpm,* the actual limit depending on the relative ionization efficiencies of the impurity and base gas. One method of improving the instrument sensitivity sufficiently to enable high-purity gases to be analysed with confidence is to operate the analyser tube at pressures of over 100 times the normally accepted working pressure of 10^{-7} torr.[1,2]

To take full advantage of this increase in sensitivity it becomes necessary to sample dynamically in order to minimize desorption errors associated with the normal gas sampling system. A system is therefore required which will sample from a gas stream, at a pressure above atmospheric, directly into the analyser tube which operates at a pressure of between 10^{-5} and 10^{-4} torr. In order to calibrate the mass spectrometer when such a sampling system is used, it is necessary to have a continuous supply of gas mixture of known composition.

Standard gas blends of nitrogen and argon,[1] containing trace amounts of helium and hydrogen respectively, have been successfully prepared by introducing small amounts of impurity into an evacuated gas cylinder, and topping up with base gas free from the impurity to be blended. This technique, however, can only be used on a limited scale, because the preparation of different blends over wide impurity ranges involves the use of far too many gas cylinders and prohibitive amounts of gases. A major disadvantage of this technique manifests itself when the base gas contains any of the impurities with which it is to be blended, thereby necessitating a high pressure purification system.

* *i.e.*, Parts per million, v/v.

Consideration was given to electrolytic methods of generating impurities in a pure gas stream, but although this is possible for generating oxygen and hydrogen for example, it obviously cannot be used for generating the inert gases. It was decided therefore to investigate the possibility of introducing, continuously, accurately known amounts of impurities into a pure gas stream by using controlled capillary leaks. This report is concerned with the design, construction and performance of a dynamic sampling and calibration system for use with a mass spectrometer, with particular reference to the analysis of high-purity helium and hydrogen.

EXPERIMENTAL

The Dynamic Sampling and Inlet System

Before any modifications to the inlet system of the mass spectrometer were carried out, the instrument performance was checked, using high analyser tube pressures in order to determine whether sufficient sensitivity could be obtained to enable the analysis of high-purity helium and hydrogen to be carried out directly (*i.e.*, without the use of impurity concentration techniques). It was found that an expansion reservoir pressure of up to 300 torr for helium and 100 torr for hydrogen could be used before any loss of ionization efficiency occurred in the analyser tube, resulting in the lowering of the intensity of impurity ion beams.* An expansion reservoir pressure of 70 torr was selected as optimum for both helium and hydrogen, since at this pressure neither gas had reached the point where the ionization efficiency was reduced by increasing the sampling pressure, and yet considerable improvement in sensitivity was afforded over the normal reservoir sampling pressure of 0·4 torr.†

Modified inlet leak and gas sampling system

The nominal value of the analyser tube inlet leak used in the MS2G sampling system is 35 lusec.‡ It is constructed of sintered silicon carbide and is supported in a short stainless steel tube. Since a pressure of 70 torr on the high pressure side of this leak gives the required analyser tube pressure, a leak some ten times smaller is necessary in order that a sampling pressure greater than atmospheric can be used. It was considered that this required leak could be most easily fabricated by partly blocking an existing one. Attempts to modify an existing leak by vacuum deposition of aluminium on to the leak face were unsuccessful and this technique was abandoned.

The method which proved successful consisted of completely covering the face of an existing leak with soft solder, removing the excess and piercing the solder with a sharp needle. With the modified leak it was found possible to sample high-purity helium and hydrogen directly from a gas stream at a pressure of approximately 800 torr, using a gas sampling system which eliminated the 2-l. glass expansion reservoir. This type of leak has been in continuous use for over two years and calibration checks over this period have shown that the instrument sensitivity remains constant to within $\pm 16\%$. The gas sampling system used in conjunction with the modified leak is shown in Figs. 1 and 2.

* The amplifier on the mass spectrometer has ten sensitivity ranges and all ion beam measurements are finally converted into range-seven readings for calculation of results. The conventional method of measuring ion beams is to denote a full scale deflection of ten divisions on the meter, when on range seven, as ten "inches". It is possible to measure an ion beam of 3000 inches by using the backing-off controls on the instrument but no provision is made for measuring beams in excess of 3000 inches.

When high analyser tube pressures are used for hydrogen, the $m/e = 1$ (H^+) ion beam is measured and the $m/e = 2$ (H_2^+) beam is calculated from it by using a previously determined ratio for $[m/e = 2]/[m/e = 1]$.

In the case of helium, no adequate reference beams exist, and so the analyser tube pressure is referred to the analyser tube ion gauge pressure as follows.

(*i*) Using the normal sampling system, measure the pressure P of helium in the sample reservoir (with a mercury manometer) which gives rise to a helium beam of 3000 inches.

(*ii*) Obtain the ion gauge pressure reading for the selected analyser tube pressure P_g.

(*iii*) The helium beam is given by $3000 \times P_g/P$ inches (assuming a linear relationship between sample reservoir pressure and helium ion beam height).

† The doser volume on the normal sampling system is approximately 1 ml and when this volume is expanded into the 2-l. reservoir the resulting pressure is about 0·4 torr.

‡ The unit "lusec" is used to describe leak-rate and 1 lusec is the rate required to raise the pressure of a 1-l. volume at the rate of 1 micron (10^{-3} torr) per sec.

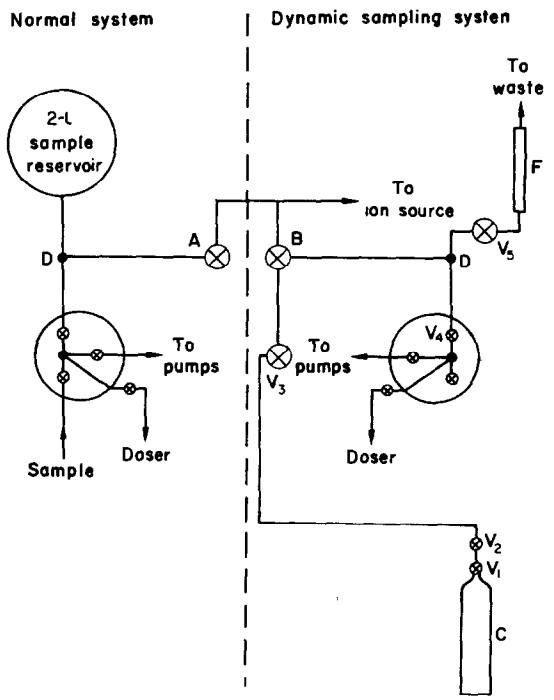

FIG. 1.—Sampling systems.

V_1—Cylinder spindle valve; V_2—gas regulator; V_3 and V_5—Edwards 1/16-in. needle valves; V_4—polythene diaphragm valve: *A*—inlet leak valve; *B*—modified inlet leak valve; *C*—test cylinder; *D*—metal flange joints; *F*—Rotameter (1–10 l/min).

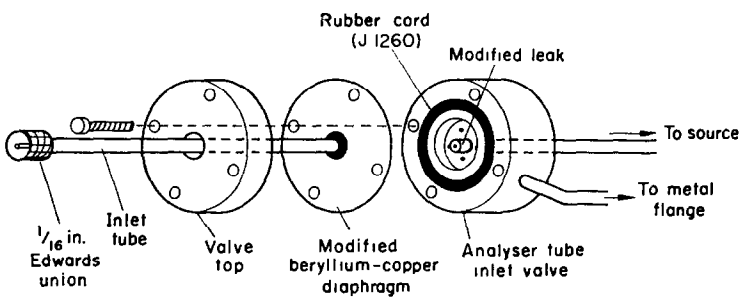

FIG. 2.—Modified analyser tube inlet leak valve.

The gas passes from the test cylinder through a gas regulator, a connecting tube and a needle valve, and then impinges directly on to the face of the inlet leak, after which it is exhausted to atmosphere *via* a second needle valve.

Cylinder helium was tested, using this dynamic sampling system with different sample flow rates, the analyser tube pressure being kept constant at $0{\cdot}5 \times 10^{-5}$ torr (as indicated by the ion gauge) by means of the two needle valves V_3 and V_5 (Fig. 1). It will be seen from the results (Fig. 3) that increasing the flow rate decreases the $m/e = 28$ ($N_2^+ + CO^+$) and $m/e = 32$ (O_2^+) readings but does not affect the $m/e = 20$ (Ne^+) reading.

The results (1, 2 and 4, Fig. 3) indicate that air is being desorbed from the rubber diaphragm in the gas regulator, and from other contaminated surfaces. To investigate this effect further, the B.O.C. gas regulator was exchanged for a Matheson type regulator employing a metal diaphragm. It will

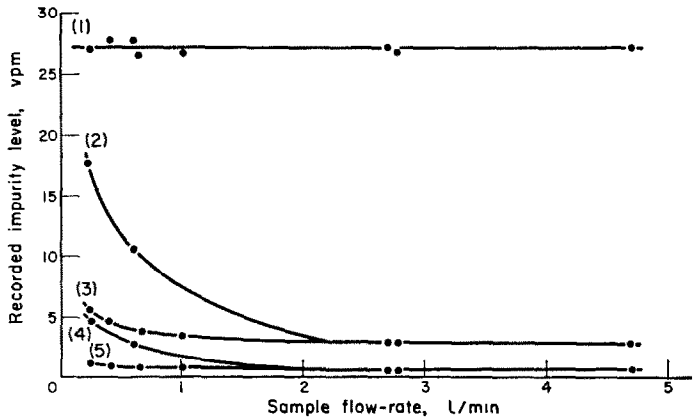

FIG. 3.—Effect of sample flow-rate on recorded impurity level.
1—m/e = 20 (Ne^+), B.O.C. and Matheson gas regulators;
2—m/e = 28 ($N_2^+ + CO^+$), B.O.C. regulator;
3—m/e = 28 ($N_2^+ + CO^+$), Matheson regulator;
4—m/e = 32 (O_2^+), B.O.C. regulator;
5—m/e = 32 (O_2^+), Matheson regulator.

be seen from the results (3 and 5, Fig. 3) that there appears to be less desorption from the metal diaphragm. At flow-rates in the region of 2–4 l/min the impurity level is independent of the type of gas regulator used.

Instrument calibration and performance at high analyser tube pressures

Known amounts of impurities (H_2, N_2, O_2, Ar and CO_2) were introduced into purified helium and hydrogen gas streams by means of a dynamic gas blending rig. With the mass spectrometer analyser tube pressure maintained at the predetermined working level, the gas blends were analysed and the impurity ion beams plotted against actual impurity content. Calibration curves for H_2, N_2, O_2, Ar and CO_2 impurities in helium and for N_2, Ar and CO_2 impurities in hydrogen were linear over the range 0–100 vpm. With oxygen in hydrogen however, the calibration deviated from a straight line and indicated an increase in sensitivity with increasing oxygen concentration. The sensitivities for these impurities are shown in Table I.

TABLE I.—INSTRUMENT SENSITIVITIES FOR IMPURITIES IN HELIUM AND HYDROGEN OVER THE RANGE 0–100 VPM

	Impurity				
	H_2	N_2	O_2	Ar	CO
Sensitivity in helium, (*in/vpm*)	0·10	0·60	0·35	0·95	0·68
Sensitivity in hydrogen, (*in/vpm*)	—	0·57	0·04–0·10	1·00	0·95

The overall precision of the new system was checked by using impure samples of helium and hydrogen contained in gas cylinders at pressures of 1500 psig and 1000 psig respectively. These samples were analysed, using the dynamic sampling system (Table II), with a flow-rate of 4 l/min and both B.O.C. and Matheson type gas regulators. The effect of using different gas regulators was shown to be negligible under the sampling conditions used.

The response time of the instrument to changes in impurity concentration, when the dynamic sampling system was used, was investigated by sampling purified helium and hydrogen *via* the dynamic gas blending rig, and suddenly introducing impurities into the gas stream by means of the rig. For impurities in helium, at the 100 vpm level, the instrument gave constant ion beam readings within 3 min. For impurities in hydrogen, the response was as good as with helium except when oxygen was the impurity. In this case the time taken to attain a constant reading was dependent on the level of impurity and could take up to 20 min (for levels greater than 100 vpm). The m/e = 18 (H_2O^+) reading also increased with increasing oxygen content, indicating that a combination reaction was

TABLE II.—REPLICATE ANALYSES

	Run	$N_2 + CO$, *vpm*	O_2, *vpm*	Ar, *vpm*	CH_4, *vpm*	CO_2, *vpm*	Gas regulator
Helium	1	107	26	1·5	22		B.O.C. (BOR 12)
	2	124	28	1·8	26		B.O.C. (BOR 12)
	3	106	26	1·4	21		B.O.C. (BOR 12)
	4	108	26	1·6	24		Matheson
	5	111	27	1·5	23		Matheson
	Mean	111	27	1·6	23		
	Std. deviation	7	1	0·2	2		
Hydrogen	1	46·0	12·2	14·9		3·1	Matheson
	2	46·0	12·2	15·0		3·0	Matheson
	3	46·3	12·7	15·2		3·0	Matheson
	4	45·8	12·2	15 0		2·9	Matheson
	5	46·2	16·3	15·0		3·0	B.O.C. (BHR 12)
	6	46·0	13·6	15·0		3·0	B.O.C. (BHR 12)
	7	45·4	13·6	15·1		3·0	B.O.C. (BHR 12)
	8	45·8	12·7	14·8		3·0	B.O.C. (BHR 12)
	9	46·5	12·7	14·9		3·0	B.O.C. (BHR 12)
	Mean	46·0	13·1*	15·0		3·0	
	Std. deviation	0·3	1·3	0·1		0·05	

* The result for oxygen, determined by using a Hersch Oxygen Meter, was 15 vpm.

taking place, probably on the tungsten filament in the ion source. The response was poor and it could take up to 45 min for the $m/e = 18$ beam to achieve a steady value. As the impurity level was lowered (by increasing the pure gas flow through the blending rig) the response time decreased. At the 5 vpm level, the response time was less than 5 sec (except for oxygen in hydrogen), and almost all of this time could be accounted for in terms of the volume of the gas blending rig and connecting pipework to the mass spectrometer.

To determine the extent of any possible combination reaction between trace amounts of hydrogen and oxygen in helium, a blend of hydrogen in helium was prepared, and analysed in the presence of varying amounts of oxygen. The results indicated that in helium containing 25 vpm of hydrogen no detectable reaction took place up to a concentration of 50 vpm of oxygen.

It was observed during routine analysis of high purity hydrogen that the $[m/e = 29]/[m/e = 28]$ ratio, *i.e.*, $^{14}N^{15}N^+/^{14}N^{14}N^+$, was approximately 0·12 which is much higher than can be expected for the natural abundance of the ^{15}N isotope. This observation can be explained if the N_2H^+ ion is produced in the ion source of the mass spectrometer when high analyser tube pressures are used. Cylinder nitrogen was introduced into a stream of purified hydrogen, and again the observed 29/28 ratio was 0·12. In an attempt to verify whether in fact the N_2H^+ ion is formed, these experiments were repeated with deuterium instead of hydrogen. In this case an ion beam at $m/e = 30$ was found, indicating the formation of the N_2D^+ ion, the $[m/e = 30]/[m/e = 28]$ ratio being approximately 0·07. Further tests were carried out with other impurities, and, although some indication of the formation of other spurious peaks were found, none of these peaks was as obvious as the $m/e = 29$ peak in hydrogen, nor did they appear at any m/e value likely to cause interference in the determination of N_2, O_2, Ar and CO_2 in hydrogen. No spurious peaks have been observed with helium at the impurity levels normally found in the high purity gas.

Application of the method to the analysis of high purity helium and hydrogen

The modified mass spectrometer, after calibration with the dynamic gas blending rig, has been used continuously for several months. Recalibration has not been found necessary except after an ion-source change, and since recalibration is normal under these conditions it is obvious that no change in procedure is involved. The life of a source filament, working under high analyser tube pressures, appears to be between six and eight months.

Because the sensitivity of the instrument is high when high tube pressures are used, variations in the analyser tube background become less important than when normal operating pressures are used (Table III). It is therefore unnecessary to measure the background before carrying out an analysis and consequently the sample throughput can be increased considerably.

Typical analyses of high purity helium and hydrogen are shown in Table IV, together with oxygen figures obtained by using a Hersch Oxygen Meter.

TABLE III.—TYPICAL ANALYSER TUBE BACKGROUND

m/e	Ion beam height, *in.*	Equivalent *vpm* (normal tube pressure)	Equivalent *vpm* (high tube pressure)
2	0·10	100	1·0
28	1·00	500	1·6
32	0·20	140	0·6
40	0·05	20	0·05
44	0·10	50	0·15

TABLE IV.—TYPICAL ANALYSES OBTAINED BY USING THE DIRECT INLET SYSTEM

Gas sample	Impurities, *vpm*					
	H_2	Ne	$N_2 + CO$	O_2*	Ar	CO_2
He–Air blend 1	<1	—	108	26(24)	2	<1
	<1	—	106	26(24)	1	<1
He–Air blend 2	<1	—	40	10(9)	1	2
	<1	—	41	10(9)	1	2
He Cyl. 1	<1	10	2	<1(2)	<1	<1
He Cyl. 2	<1	9	5	1(2)	<1	<1
He Cyl. 3	<1	9	3	1(1)	<1	<1
He Cyl. 4	<1	9	4	1(1)	<1	<1
He Cyl. 5	1	7	26	6(6)	<1	<1
He Cyl. 6	1	8	30	6(6)	<1	<1
He Cyl. 7	<1	9	3	<1(1)	<1	<1
He Cyl. 8	<1	9	2	1(1)	<1	<1
H_2 Cyl. 1	—	—	37	— 6(5)	1	<1
	—	—	39	6(5)	<1	<1
H_2 Cyl. 2	—	—	12	1(—)	<1	<1
	—	—	15	1(—)	<1	<1
H_2 Cyl. 3	—	—	26	6(5)	1	1
H_2 Cyl. 4	—	—	43	9(—)	1	6
H_2 Cyl. 5	—	—	30	1(1)	1	<1
H_2 Cyl. 6	—	—	15	1(2)	1	<1
H_2 Cyl. 7	—	—	13	1(1)	<1	<1
H_2 Cyl. 8	—	—	22	1(1)	1	<1

* Oxygen results in brackets were obtained with a Hersch Oxygen Meter.

The Dynamic Gas Blending Rig

Gas purification

Before work was started on a blending rig, it was considered necessary to have a gas purification unit capable of providing a supply of both pure helium and pure hydrogen, because the analysis of these gases was of prime importance. Several systems were considered, and the one finally adopted as being the simplest with the necessary efficiency consisted of a glass U-tube, packed with 35 g of active carbon (type C, Sutcliffe, Speakman and Co. Ltd., Leigh, Lancs., U.K.), cooled in liquid nitrogen. This purification unit was found to remove H_2, N_2, O_2, Ar and CO_2 from helium, and N_2, O_2, Ar and CO_2 from hydrogen, at flow-rates of up to 3 l/min. The capacity of the purifier for hydrogen was 10·6 ml (at S.T.P) per g of charcoal. After purification, the sum total of these impurities, in both helium and hydrogen, was approximately 1 vpm. The carbon can be regenerated *in situ* by evacuation for several hours at room temperature or for about 1 hr at 100°C.

Mass spectra of purified helium and hydrogen, together with their respective backgrounds, are

shown in Fig. 4. It will be observed that in the case of hydrogen a group of peaks appear in the m/e = 28 and m/e = 44 regions. These peaks may be due to the formation of hydrocarbons by reaction of hydrogen with carbon from the tungsten filament in the ion source. Prolonged conditioning of the filament (several days) reduced these spurious peaks to below 0·5 in. although it should be noted that, at the high analyser tube pressures used, these peaks represent less than 1 vpm of impurity.

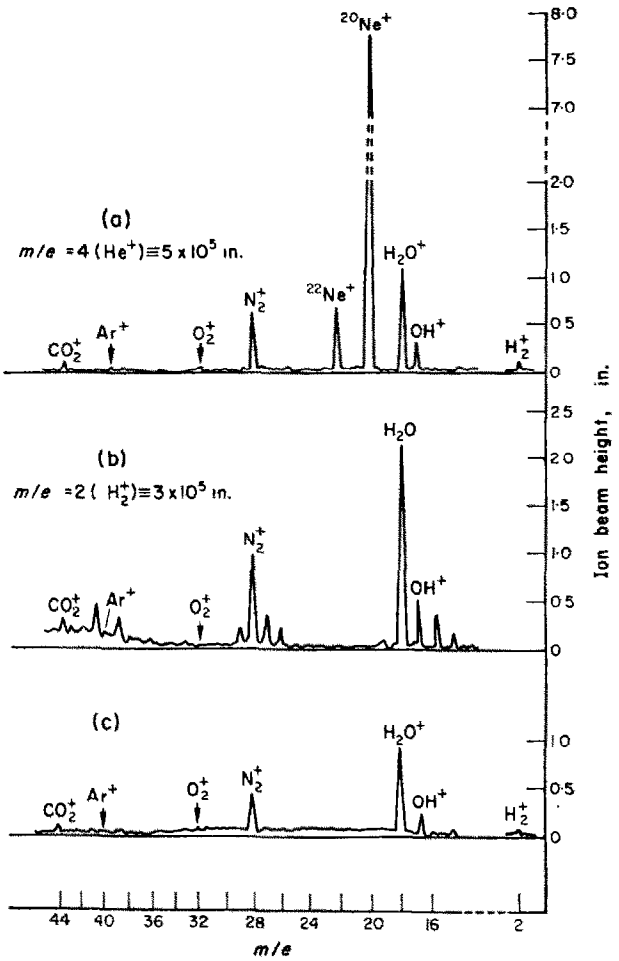

FIG. 4.—Mass spectra of purified (*a*) helium, (*b*) hydrogen, and (*c*) tube background.

Introduction of impurities into a gas stream by the use of fine bore capillary leaks

Preliminary work in which an impurity gas, under pressure, was allowed to enter a pure gas stream *via* a fine bore capillary leak (internal diameter 0·04 mm; length 30 cm) indicated that an impurity gas flow-rate of between 0·08 and 0·20 μl/min/torrΔP* could be realized, depending on the nature of the impurity. Hence, by maintaining a differential pressure of say 50 torr across the leak, and a pure gas flow-rate of 3 l/min, blends containing between 1·3 and 3·3 vpm of an impurity could be prepared.

Experiments were carried out to determine the short and long term stability of the capillary leak.

Short term stability. A stream of argon-free hydrogen was passed through a mixing chamber containing the capillary leak. Argon was passed through this leak under a constant differential pressure

* When the absolute pressure on the impurity side of the leak is greater than the absolute pressure in the pure gas stream, there is considered to be a positive differential pressure (ΔP) across the leak.

(ΔP) of 60 torr and entered the hydrogen stream. The resulting gas mixture, containing approximately 13 vpm of argon, was monitored continuously for argon content with a mass spectrometer fitted with the direct inlet leak previously described. The results showing variation of recorded impurity level with time are shown in Fig. 5. It will be seen that the blend remained constant within $\pm 4\%$ over a period of approximately 7 hr. It should be noted that this test indicates not only the stability of the capillary leak used for blending, but also of the modified mass spectrometer leak, and any other variable in the system.

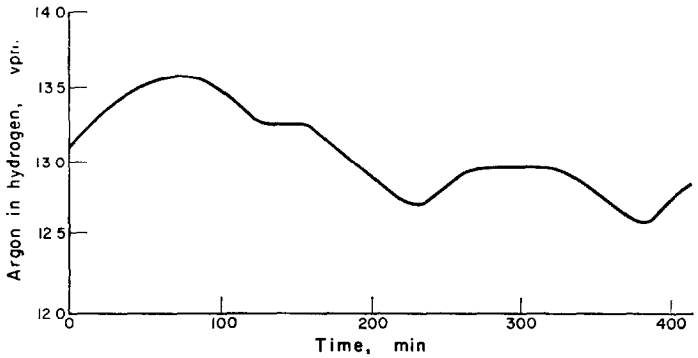

FIG. 5.—Variation of recorded impurity level with time.

Long term stability. The long term stability of the leak was checked by noting, a number of times over a period of several weeks, the time taken for the differential pressure in a reservoir (approximately 7 ml in volume) supplying the leak, to fall from 400 torr ΔP to 200 torr ΔP. Hydrogen was used as the test gas in these experiments. The results in Table V show the long term stability to be better than $\pm 4\%$ over a period of 50 days.

TABLE V.—LONG TERM STABILITY OF THE CAPILLARY LEAK

Time interval between tests, *days*	Temperature, °C	Time taken for ΔP to fall from 400 torr to 200 torr, *min*
0	25	32·4
1	28	33·8
23	25	32·0
29	26	31·4
36	26	32·5
42	25	32·2
50	25	31·5
	Mean	32·3
	Std. devn.	0·8

On the basis of these results it was decided to build a practical blending rig (Fig. 6) incorporating the following necessary requirements.

(*i*) Simple and rapid interchange of leaks, when necessary.

(*ii*) Ease of measurement of the absolute pressure (P) in the pure gas stream at the point where the impurity is introduced.

(*iii*) A means of determining and controlling the differential pressure (ΔP) across the leak, (*i.e.*, the pressure difference between the impurity reservoir and the pure gas stream).

(*iv*) Control and measurement of the pure gas flow-rate (F).

For maximum accuracy a thermostat should also be incorporated in the apparatus. However, in the author's laboratory, errors due to temperature variations were considered to be sufficiently small to render such a refinement unnecessary.

The gas mixing chamber and leak assembly. The gas mixing chamber is shown in detail in Fig. 7. and is fabricated from copper tubing and Edwards hand-tight unions. Provision is made for the inlet and outlet of pure gas, measurement of the gas stream pressure, and attachment of the capillary leak assembly. The leak assembly is shown in detail in Fig. 8. It is designed so that the capillary can be firmly held in position during assembly and use, and easily dismantled for leak changes.

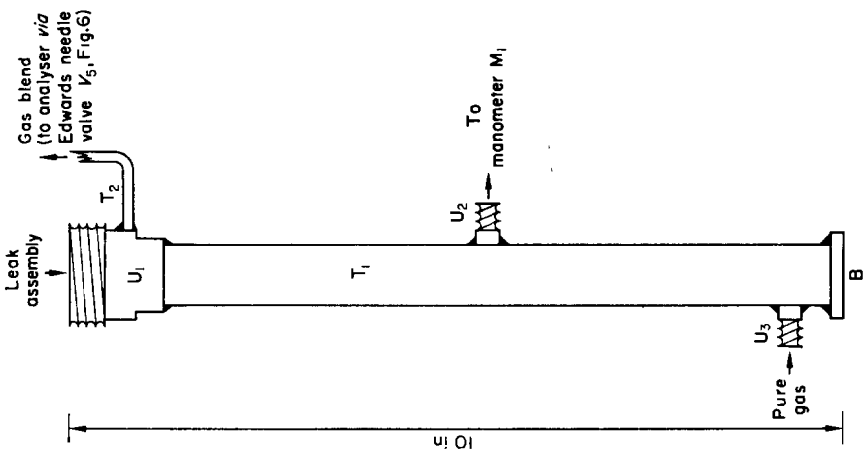

FIG. 7.—The gas mixing chamber.
B—Brass blanking off disc; T_1—3/4-in. nominal bore copper tube; T_2—1/16-in. nominal bore stainless steel tube; U_1—3/4-in. male thread Edwards union; U_2 and U_3—1/16-in. male thread Edwards unions.

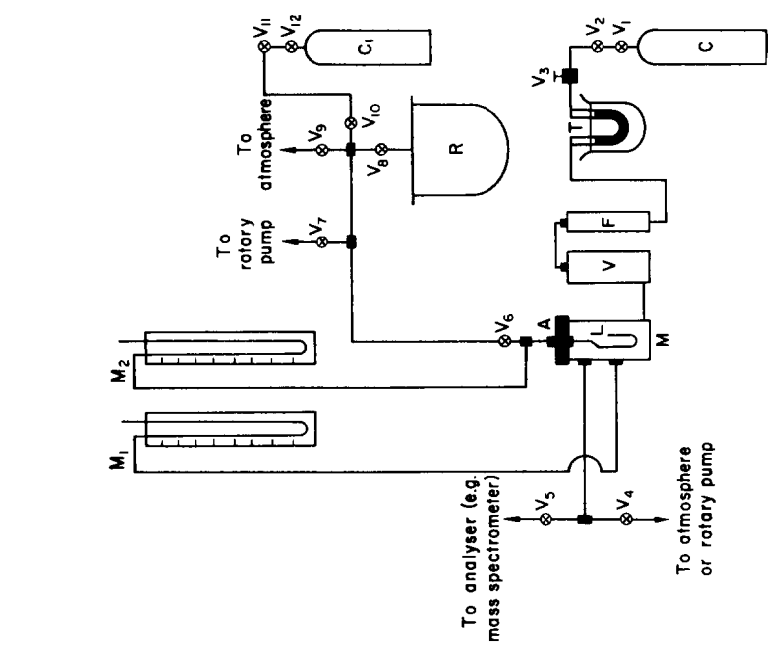

FIG. 6.—Schematic diagram of dynamic gas blending rig and purification unit.
A—Leak assembly; *C*—cylinder of base gas; C_1—cylinder of impurity gas; *F*—Rota meter (0·1–1·0 l/min); *L*—capillary leak; *M*—mixing chamber; *R*—impurity gas reservoir (~4 l.); *T*—purification unit; *V*—ballast volume; M_1 and M_2—mercury-filled manometers: V_1 and V_{12}—cylinder spindle valves; V_2 and V_{11}—gas regulators; V_3 vacuum pressure controller (Edwards type VPC 1); V_4, V_5, V_8, V_9, V_{10}—Edwards 1/16-in. needle valves; V_6, V_7, V_8—1/4-in. Edwards Saunders valves.

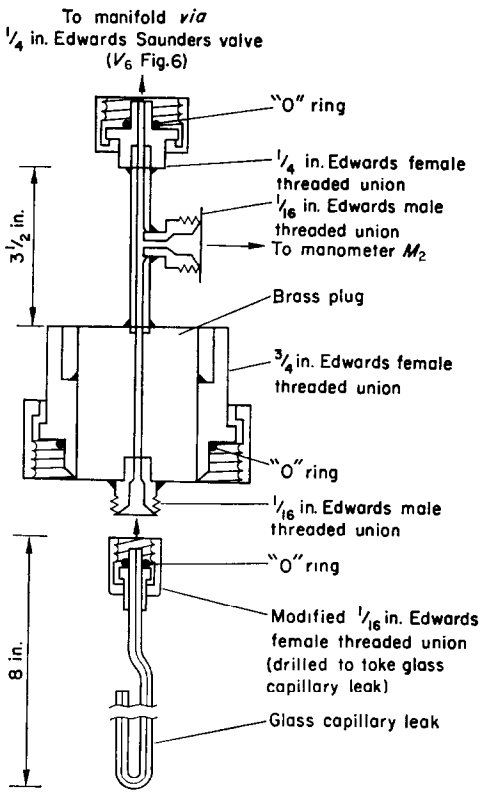

FIG. 8.—Section through the leak assembly.

Measurement of absolute pressure of the pure gas stream in the mixing chamber and differential pressure across the leak. Both these measurements were accomplished by using the manometers M_1 and M_2 shown in Fig. 6. The absolute pressure in the mixing chamber is given by the reading on M_1 plus the atmospheric pressure. The differential pressure is given by the reading on M_2 minus the reading on M_1. It was decided to operate the gas blending rig with an absolute pressure of 1000 torr in the mixing chamber, so as to ensure that an adequate pressure was available for the mass spectrometer dynamic sampling system, or any other detector which was to be calibrated.

Flow and pressure control of the pure gas stream. Control of the pure gas flow-rate (F) and pressure (P) was accomplished by manipulation of the two needle values V_4 and V_5 and the vacuum pressure controller V_3, Fig. 6. The pure gas flow-rate was measured with a Rotameter, 0·1–1 l/min, which was calibrated for each gas used by operating the blending rig at the selected mixing chamber pressure of 1000 torr and measuring the flow of gas at atmospheric pressure by a soap-bubble flowmeter, and converting this flow-rate into a flow-rate at 1000 torr.

The Rotameter was inserted in the apparatus at a point before the mixing chamber so that variations in atmospheric pressure did not have to be taken into account, since the absolute pressure in the mixing chamber is constant, and controlled at 1000 torr.

The complete apparatus was assembled in a perspex box filled with a colourless mineral oil which completely covered the mixing chamber, ballast chamber, and almost all of the impurity reservoir.

Calibration and operation of the dynamic gas blending rig

The volume* contained between V_6 (Fig. 6), the manometer M_2 and the leak assembly was raised in pressure to 1600 torr absolute, with the test gas *via* V_6. With V_6 closed, and the mixing chamber

* This volume (approximately 7 ml) is kept as small as is practically possible, so as to speed up the calibration procedure. It must be measured accurately, and corrections should be made for the change in volume which occurs due to the mercury rising in the arm of M_2 as the pressure falls during calibration.

pressure maintained at 1000 torr, the differential pressure (ΔP) across the leak was noted at time intervals of 5–10 min, down to a ΔP of 50 torr.

A plot of $d(\Delta PV)/1000\,dt$ against ΔP, where t is the time, will then show the variation of flow-rate (at 1000 torr) through the leak as ΔP is varied. Hence by noting ΔP across the leak, and the pure gas flow-rate through the mixing chamber, the compositions of the blend can be readily calculated.

The term $d(\Delta PV)/dt$ can be obtained from a plot of ΔPV against t by determining the gradient at different values of ΔP, or by calculating it as follows:

If ΔP_1V_1 = the product of differential pressure and volume at time t_1

and ΔP_2V_2 = the product of differential pressure and volume at time t_2

Then $\dfrac{d(\Delta PV)}{dt}$ at pressure ΔP is given by $\dfrac{(\Delta P_1V_1) - (\Delta P_2V_2)}{(t_1 - t_2)}$

where $\Delta P = \dfrac{\Delta P_1 + \Delta P_2}{2}$.

The latter method is recommended since it eliminates any personal error associated with choosing a gradient at a point, and is reasonably accurate providing the time intervals are relatively small, and the differential pressures are carefully measured. This procedure is repeated for each impurity gas which is required for blending purposes.

When the gas blending rig is in use, V_6 and V_8 (Fig. 6) are opened so that the reservoir R supplies the leak, hence maintaining an essentially constant ΔP across the leak and therefore a constant blend. This is required, of course, when calibrating the mass spectrometer or any other detector.

Performance of the gas blending rig

The precision attainable with the gas blending rig was determined by preparing blends of argon in hydrogen at the 13 vpm level. The blends were prepared with a wide range of differential pressures and pure gas flow-rates, adjusted so that the argon ion beam recorded by the mass spectrometer was kept constant. The blends were then calculated, and the results are shown in Table VI.

TABLE VI.—PRECISION OF THE GAS BLENDING RIG

Indicated flow-rate of hydrogen, *l/min*	Actual flow-rate of hydrogen, *l/min*	ΔP, *torr*	Argon flow-rate, *μl/min*	Argon, *vpm*
0·800	2·356	481	32·2	13·7
0·700	2·062	426	27·5	13·3
0·600	1·719	369	23·1	13·4
0·500	1·427	312	18·8	13·2
0·400	1·115	248	14·4	12·9
0·300	0·783	184	10·4	13·3
0·200	0·505	119	6·5	12·9
0·100	0·242	59	3·2	13·2
			Mean	13·2
			Std. deviation	0·27

To investigate the accuracy of the analysis system (*i.e.*, the dynamic gas blending rig and the mass spectrometer), two high pressure gas blends of impurities in helium (X and Y) were prepared and stored in cylinders at approximately 1000 psig. Both blends were analysed with a mass spectrometer which had previously been calibrated with the dynamic gas blending rig. These results are shown in Table VII.

Blend Y was also analysed at the Research Laboratories of the British Oxygen Company. Table VIII shows the comparison between their results and ours, together with the methods that were used for each determination.

The instruments (B.O.C.) were calibrated with Wosthoff metering pumps except for the Elcoflux oxygen analyser which has a built-in electrolytic calibration unit.

Gas recirculation system

In order to conserve supplies of helium when calibrating the mass spectrometer, a recirculating system (Fig. 9) was used. The purified gas was passed through the blending rig where it picked up a known amount of impurity. This blend was analysed by the mass spectrometer and was then returned

TABLE VII.—COMPARISON OF CYLINDER BLENDS WITH MASS SPECTROMETRIC ANALYSES

Blend	Impurity	Calculated composition of blend, *vpm*	Mass spectrometric results, *vpm*
X	H_2	24·3	27·5
	$N_2 + CO$	138	138
	O_2*	12·5	13·6
	Ar	25·0	24·4
	$CO_2 + N_2O$	13·0	13·8
Y	H_2	12·4	11·7
	$N_2 + CO$	22·6	23·0
	O_2*	5·7	5·4
	Ar	—	0·2
	CO_2	8·2	9·3

* The oxygen contents of the two blends, determined with a Hersch Oxygen Meter, were *X*, 14·4 vpm; *Y*, 5·9 vpm.

TABLE VIII.—COMPARISON OF RESULTS

British Oxygen Company			Chemical Inspectorate mass spectrometric analysis, *vpm*
Method of analysis	Impurity	Results, *vpm*	
Palladium chloride assay	H_2	10	11·7
Gas chromatography (Lipsky detector)	$N_2 + CO$	25	23·0
Elcoflux analyser	O_2	7	5·4
Mass spectrometer	Ar	0·5	0·2
Wosthoff analyser	CO_2	8	9·3

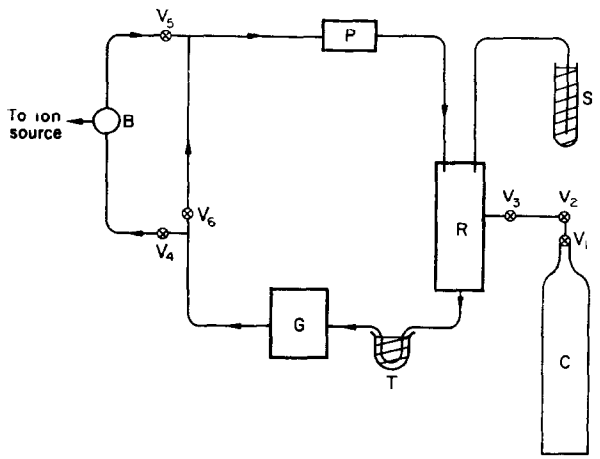

FIG. 9.—Schematic diagram of recirculation system and mass spectrometer direct inlet system.

B—Mass spectrometer direct inlet valve; *C*—base gas cylinder; *G*—dynamic gas blending rig; *P*—recirculating pump; *R*—base gas reservoir (~4·1); *S*—mercury blow-off; *T*—purification unit; V_1—cylinder spindle valve; V_2—gas regulator; V_3—1/4-in. Edwards Saunders valve: V_4, V_5 V_6—1/16-in. Edwards needle valves.

to the purification unit *via* a recirculating pump. An Edwards oil-filled rotary pump (Type 1SC 50.B) and a Genevac vacuum-compressor pump (Type RPC.2) were both used successfully as recirculating pumps, the latter being more satisfactory because of its small size.

Applications of the Dynamic Sampling System, Dynamic Gas Blending Rig, and Gas Recirculation System

Apart from the analysis of high-purity helium and hydrogen already described, the mass spectrometer, fitted with the dynamic sampling system, has been used as a detector for a gas chromatograph. For example, by using a column packed with Linde molecular sieve type 5A at approx 50°C and feeding the helium carrier gas to the mass spectrometer (tuned at maximum sensitivity on the $m/e = 28$ ion beam), it was possible to detect 0·5 vpm of CO in a 10-ml sample of hydrogen, and to determine CO in hydrogen at the 5 vpm level with a standard deviation of 0·2 vpm. It has also been used for investigations into the determination of hydrocarbons in helium at the 5 vpm level by oxidation to CO_2, where continuous monitoring of reaction products was necessary.

The dynamic gas blending rig has been used for the calibration of mass spectrometers, catharometer detectors and gas chromatographs, and also for studying the characteristics of a helium ionization detector.[3] It has also been used successfully for the preparation of certain gas mixtures at the 0·1 vpm level, by diluting the required impurity with another gas of approximately the same molecular weight and viscosity (hence minimizing any fractionation effects) and feeding this binary mixture through the calibrated leak. Examples are N_2O and CO_2 mixtures for preparing blends of N_2O in hydrogen, and CO and N_2 mixtures for preparing blends of CO in helium and hydrogen.

Gas recirculation systems have been used to conserve supplies of purified helium on gas chromatographs, the carrier being exhausted to atmosphere only when samples were being analysed. This has resulted in the use of about 1/7 of the amount of high-purity helium that would have been needed for a system permanently exhausted to atmosphere.

Acknowledgement—I would like to acknowledge the co-operation of Mr. J. H. Scawin (Operational Services Dept.,) and Mr. J. Pennington (Rare Gas Dept.,) both of the British Oxygen Company Ltd., who agreed to carry out the analysis of one of the cylinder blends, and who also gave permission for the results to be included in this report.

Zusammenfassung—Ein dynamisches Gaseinlaßsystem für ein Massenspektrometer (A.E.I. Modell MS2G) wurde entworfen. Es kann Proben direkt aus Gasströmen bei Drucken um 800 Torr entnehmen und wurde mit Erfolg bei der Analyse von hochreinem Helium und Wasserstoff mit weniger als 50 vpm (1 vpm = Volumenanteil 10^{-6}) gesamter Verunreinigung benutzt. Die Empfindlichkeit ist 1 vpm oder besser. Das System ist so augselegt, daß das Massenspektrometer bei Bedarf mit seinem normalen Gaseinlaßsystem benutzt werden kann. Zur Eichung des Massenspektrometers im Bereich 5–100 vpm Verunreinigung wirde eine dynamsiche Gasmischbatterie entwickelt, die ein Umlauf- und Reinigungssystem enthält.

Résumé—On a conçu un système d'échantillonnage de gaz dynamiques pour utilisation avec un spectromètre de masse (A.E.I. Modèle MS2G). Il est capable d'échantillonner directement à partir de courants gazeux à des pressions situées dans la zone de 800 torr et a été utilisé de façon satisfaisante pour l'analyse d'hélium de haute pureté et d'hydrogène

contenant moins de 50 p.p.m. (v/v) d'impuretés totales. La sensibilité globale est égale à 1 p.p.m. (v/v) ou meilleure. Cet appareillage permet l'emploi du spectromètre de masse avec son système d'échantillonnage de gaz normal si nécessaire. Une installation de mélange de gaz dynamiques, comprenant un système de recirculation et de purification, a été élaborée pour l'étalonnage du spectromètre de masse dans le domaine de 5–100 p.p.m. (v/v) de teneur en impuretés.

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RADIOACTIVE SUBSTOICHIOMETRIC ISOTOPE-DILUTION PROCEDURE FOR THE DETERMINATION OF RARE EARTH METALS

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Summary—A theory is developed which describes the equilibrium conditions when solutions containing trace metals and substoichiometric amounts of EDTA are extracted with thenoyltrifluoroacetone. Experimental evidence is given to support the theory. A method for the determination of microgram quantities of rare earth metal is outlined as an application.

ANALYSIS for trace quantities of metals, by activation analysis or radioactive isotope-dilution analysis, can be simplified by using the technique of substoichiometry. Equal quantities of metal are removed from the active standard and treated sample solutions by a known amount of complexing agent which is insufficient to react with all the metal present. The separated fractions are then compared. In this way, the need for chemical yield determination is avoided, and selectivity improved.[1]

Most substoichiometry has been performed by solvent extraction with strong chelating agents. Extraction of ion-association complexes has been used[2,3] and also the reaction with EDTA, followed by removal of excess of metal by ion-exchange.[4,5,6]

Of these methods, the first is the most straightforward. The last, EDTA reaction, can become very involved when applied to the general case. Unlike the solvent extraction method, optimum conditions have to be calculated for two reactions, the complexation and the exchange of excess of metal with the resin. In the first case, all the EDTA present must react, and in the second, no EDTA complex must be involved in the exchange. The choice of pH, and the nature and strength of the buffer for the first reaction, all have a marked effect on the ion-exchange. For example, acetate buffers, commonly used for EDTA reactions, themselves complex many metals sufficiently to prevent efficient exchange, unless they are very dilute. At large dilutions the ionic strength of the solution is a critical factor.

In this paper, the simpler case is dealt with, in which the excess of metal is removed by solvent extraction, using a weaker complexing agent than EDTA.

The system containing rare earth, EDTA, and thenoyltrifluoroacetone was studied. A possible method for the determination of microgram quantities of rare earth after separation by ion-exchange was developed.

THEORY

There are two reactions to consider.

1. Rare earth (M) plus thenoyltrifluoroacetone (HA).
2. Rare earth (M) plus EDTA (Y).

$$M + 3HA_{org} \rightarrow (MA_3)_{org} + 3H \quad (1)$$

$$M + Y \rightarrow MY \quad (2)$$

The subscript "org" indicates solution in an organic solvent immiscible with water. Electrical charges are omitted for simplicity.

The following theory makes use of the idea of conditional equilibrium constants, in a similar way to the work of Schwarzenbach and Ringbom.[7] This means that the equilibrium concentration [X] of any species, is replaced by the total amount present in any form [X']. The equation must be modified by a so-called α coefficient given by

$$\alpha = \frac{[X']}{[X]}. \tag{3}$$

Equilibrium constants calculated in this way are not really constant, but depend on the conditions used: hence the name conditional constant.

The extraction constant from equation (1) is

$$K_1 = \frac{[MA_3]_{org}[H]^3}{[M][HA]^3_{org}}. \tag{4}$$

The stability constant from equation (2) is

$$K_2 = \frac{[MY]}{[M][Y]}. \tag{5}$$

Instead of K_2 we use K_3, the conditional constant:

$$K_3 = \frac{[MY]}{[M][Y']} \tag{6}$$

where [Y'] is the total equilibrium concentration of EDTA in all its forms, *i.e.*, $[Y'] = [H_4Y] + [H_3Y] + [H_2Y] + [HY] + [Y]$ (again with charges omitted).

Then

$$\frac{[Y']}{[Y]} = \alpha_Y$$

and

$$K_2 = \frac{[MY]\alpha_Y}{[M][Y']}. \tag{7}$$

By combining equations (4) and (7):

$$K_4 = \frac{K_1}{K_2} = \frac{[MA_3]_{org}[H]^3[Y']}{[MY][HA]^3_{org}\alpha_Y}. \tag{8}$$

Assuming that a reaction equilibrium is reached, let us take the case where half of the metal present is complexed to form MY, *i.e.*, 50% stoichiometry; HA removes the remainder, which becomes transferred to the organic phase. It must be remembered that this paper follows the terminology of previous authors, *i.e.*, x% stoichiometry or substoichiometry refers to the relative amounts of the reacting species, that is the degree to which one is equivalent to the other. The actual reaction is assumed to be stoichiometric.

Under these conditions, and when the volumes of both phases are equal,

$$[MY] = [MA_3]_{org}$$

and equation (8) simplifies to:

$$K_4 = \frac{[H]^3[Y']}{[HA]_{org}^3 \alpha_Y}. \tag{9}$$

$[HA]_{org}$ is not a simple term, for two reasons. First HA dissociates, $HA \rightleftharpoons H + A$, the constant for the reaction being

$$K_{diss} = \frac{[H][A]}{[HA]}, \tag{10}$$

and secondly, HA is not entirely in the organic phase. The partition is described by:

$$P_{HA} = \frac{[HA]_{org}}{[HA]}. \tag{11}$$

Dividing equation (10) by equation (11):

$$\frac{K_{diss}}{P_{HA}} = \frac{[H][A]}{[HA]_{org}}. \tag{12}$$

Let us call the sum of the concentrations of all the forms of HA present, [HA']. In the case already mentioned, where the phases have equal volumes, [HA'] is in fact the concentration added in the organic phase at the start of the reaction, providing there is no association or polymerization in either phase.

Then

$$[HA'] = [HA]_{org} + [HA] + [A]$$

or

$$\frac{[HA']}{[HA]_{org}} = 1 + \frac{[HA]}{[HA]_{org}} + \frac{[A]}{[HA]_{org}} \tag{13}$$

and we can call this α_A:

$$\alpha_A = 1 + \frac{1}{P_{HA}} + \frac{K_{diss}}{P_{HA}[H]}. \tag{14}$$

From a knowledge of the partition coefficient and the dissociation constants, α_A can be calculated. The result is conveniently shown in graphical form in Fig. 1.

Equation 9 becomes

$$K_4 = \frac{[H]^3[Y']\alpha_A{}^3}{[HA']^3\alpha_Y}. \tag{15}$$

An essential condition of substoichiometry is that all the reagent must be consumed by the metal. As a practical condition, this is taken to be true if $[Y'] < 0{\cdot}001\ C_{HY}$, where C_{HY} is the concentration of EDTA that would be present if no reaction had taken place.

Thus

$$K_4 = \frac{[H]^3 \,.\, 10^{-3} C_{HY} \alpha_A{}^3}{[HA']^3 \alpha_Y}. \tag{16}$$

From this equation can be calculated a value of [HA'] for a particular EDTA reaction. It represents the maximum concentration of HA which may be used to remove free metal from a solution in which a substoichiometric reaction with EDTA

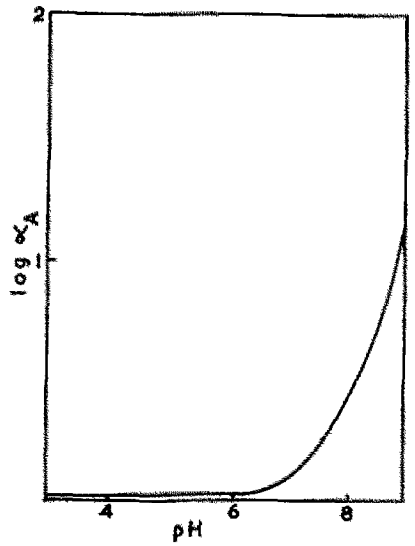

Fig. 1.—Variation of the conditional constant for thenoyltrifluoroacetone with pH.

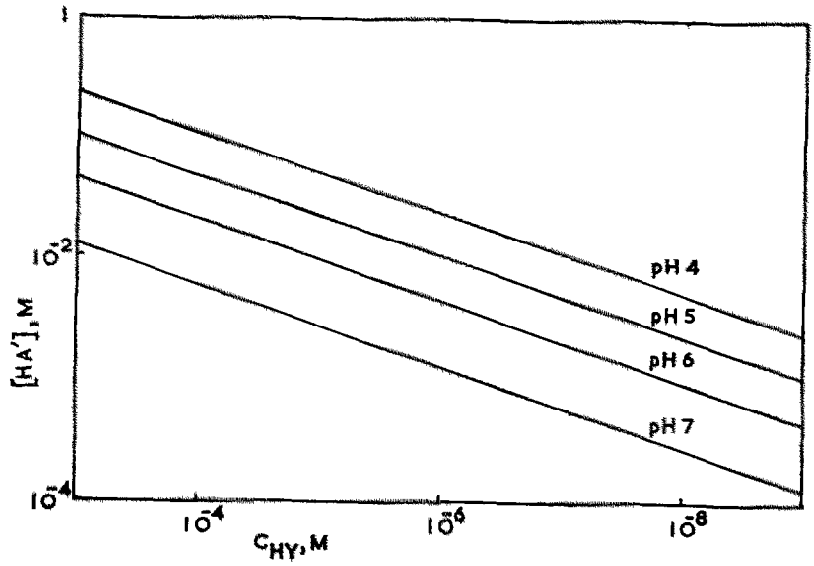

Fig. 2.—Influence of hydrogen-ion concentration on the maximum concentration of thenoyltrifluoroacetone which may be used to remove free metal from a metal–EDTA complex. Calculated for terbium.

is taking place, without breaking down more than 0·1% of the EDTA complex. A further condition is that $[HA'] \gg [MA_3]$ so that the change of concentration on reaction is negligible. This will be true for a weak complexing agent. Figure 2 shows how this value of [HA'] varies with pH for fixed concentrations of C_{HY}. The values given are calculated for terbium. Figure 3 shows how this graph is affected, at any one EDTA concentration, by the choice of metal. Like many other rare earth properties, the equilibrium constants for both these reactions, *i.e.*, K_1 and K_2, vary as the atomic

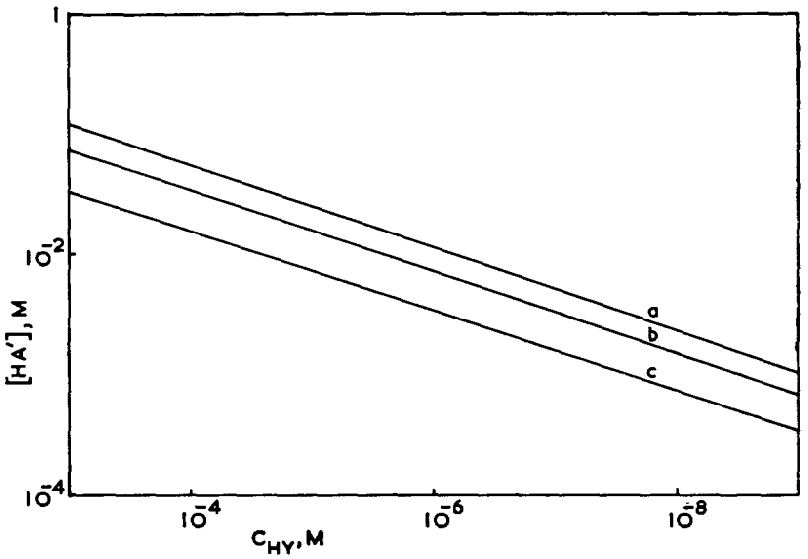

FIG. 3.—Influence of rare earth metal at a fixed pH on the maximum concentration of thenoyltrifluoroacetone which may be used to remove free metal from a metal-EDTA complex. *a*. Calculated for lutetium at pH 6. *b*. Calculated for lanthanum at pH 6. *c*. Calculated for gadolinium at pH 6.

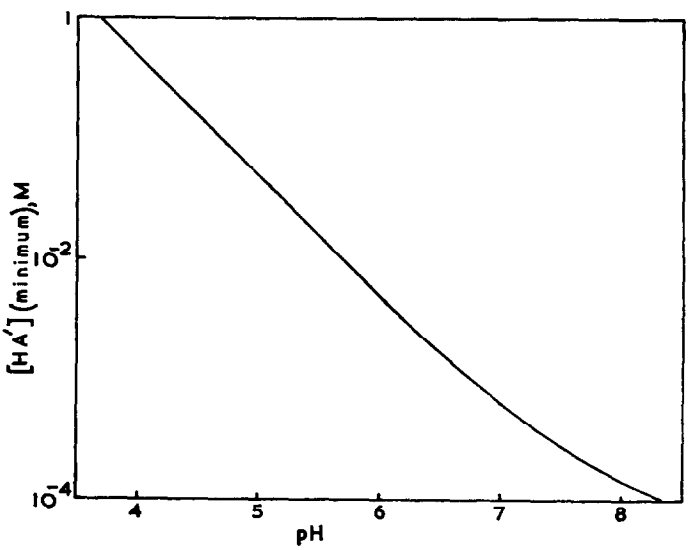

FIG. 4.—The minimum excess of thenoyltrifluoroacetone required for the extraction of rare earth metal at various pH values. Calculated for terbium.

number increases. The trends are different in each case, resulting in a maximum value of K_4 at gadolinium, in the middle of the series.

The minimum excess of HA required can be determined from equation (4), and the case of terbium is again illustrated in Fig. 4. Extraction is assumed to be complete when $[MA]_3/[M] = 1000$.

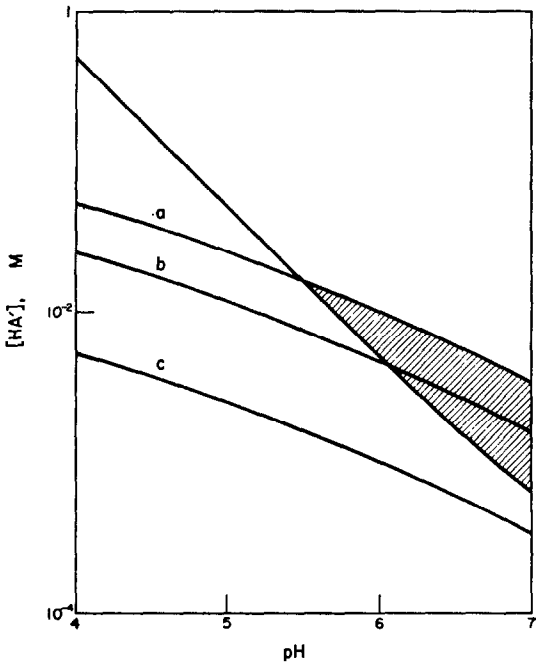

FIG. 5.—The working range of thenoyltrifluoroacetone concentration for removal of excess metal from metal–EDTA complex. *a*. $C_{HY} = 10^{-5}M$ *b*. $C_{HY} = 10^{-6}M$ *c*. $C_{HY} = 10^{-8}M$. All calculated for terbium. The working range is shaded.

If the information contained in Fig. 2 is superimposed on Fig. 4 the result is a graph which gives the working range of HA concentration, for any pH, which can be used to remove excess of metal from a solution in which substoichiometry has been performed with EDTA, without affecting the EDTA complex (Fig. 5).

Two very important assumptions have been made and require investigation. At high dilutions the metal being determined must react with HA according to equation (4). Equation (8), being the basis of further calculations, must be verified.

These experiments present no difficulty. If a dilute solution of rare earth metal is extracted with a solution of thenoyltrifluoroacetone, stoichiometrically in large excess, but still too dilute to extract all the metal, the logarithmic plot of q = [metal in org. phase]/[metal in aqueous phase] *vs.* [HA'] should be linear and have a slope of +3. This was found to be the case. The correct value of K_1 at this dilution is also determinable from the intercept.

Verification of equation (8) can be achieved in a similar way. Consider the case where all the EDTA present is just sufficient to complex all the metal, but the HA present in the organic phase is strong enough to partly decompose the EDTA complex.

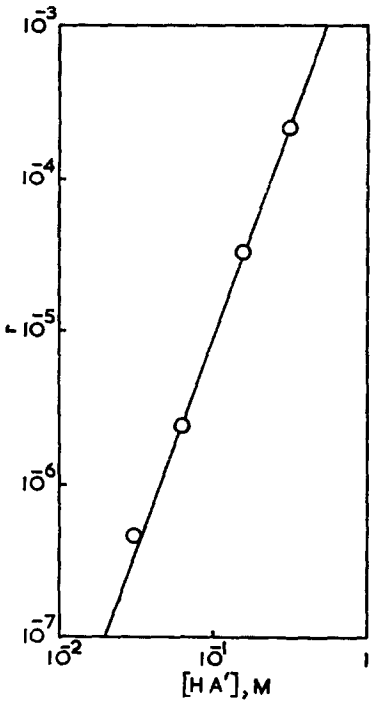

FIG. 6.—Experimental verification of equation (8).

$$r = \frac{[\text{metal in organic phase}]^3}{[\text{metal in aqueous phase}]}.$$

Any MA_3 (or free EDTA) present can be assumed to come from the decomposition of MY. Hence $[MA_3] = [Y']$.

Thus, introducing the α_A term into equation (8) and rearranging

$$\frac{K_4\alpha_Y}{[H]^3\alpha_A{}^3} = \frac{[MA_3]^2_{org}}{[MY][HA']^3}. \tag{17}$$

That is, a logarithmic plot of $r = [\text{metal in org. phase}]^2/[\text{metal in aqueous phase}]$ *vs.* [HA'] should be linear and of slope +3, having an intercept of $K_4\alpha_Y/[H]^3\alpha_A$. This was also found to be true (Fig. 6).

It was also observed that the reaction between HA and free metal came to equilibrium many times faster than the decomposition of metal–EDTA complex by HA. This is itself an important factor when considering the development of an analytical method.

EXPERIMENTAL

Reagents

Buffer solution. The choice of buffer, which must be suitable for both the EDTA reaction and the extraction, was a little difficult. The one finally used was 1*M* hexamine, adjusted to the required pH with nitric acid. Only laboratory-reagent grade hexamine was available and it was thought that further trouble might arise from metallic impurities in it. In the simplest case these would give rise to a large reagent blank, although much more complicated interferences can be envisaged. These interferences did not occur, at least not at the concentrations used in the experiments. At very large dilutions there are several other factors which may cause difficulty. These are outlined below.

All other reagents were of analytical-reagent grade purity.

Rare earth solutions were prepared by dissolving the oxide or the nitrate in nitric acid or water respectively. Whenever possible, relatively concentrated solutions were made and standardized against EDTA, before being diluted to the required trace concentration.

Water was twice distilled from glass. Tracer and isotope-dilution experiments were carried out with ^{141}Ce, ^{160}Tb and ^{170}Tm.

Apparatus

The detector used was a 1·75 in. × 2 in. NaI(Tl) well-type crystal: well-volume 5 ml. This was associated with a single channel gamma-ray spectrometer. Discriminator settings were used to give the highest possible counting efficiencies.

Verification of equations (4) *and* (8)

Equation (4). A series of labelled terbium test solutions was prepared by diluting 1 ml of a $10^{-5}M$ stock solution with 9 ml of hexamine buffer at pH 6. Each test solution was extracted with 10 ml of a xylene solution of thenoyltrifluoroacetone of concentrations varying from $10^{-4}M$ to $10^{-3}M$, until equilibrium was reached. The activity of 5 ml of both aqueous and organic phases was measured and the final pH noted. The results gave a slope of 2·9. This corresponds to a value of K_1 of $10^{-8.25}$. An assumed slope of 3·0 gives a K_1 value of $10^{-8.1}$ for all but very low q values.

Equation (8). A stock solution of rare earth plus EDTA was prepared by mixing 25 ml of a $10^{-3}M$ labelled terbium solution with an equivalent amount of EDTA solution, neutralizing to pH 4·5 and making up to 50 ml. For the purpose of this experiment it was assumed that this solution was a pure solution of terbium–EDTA complex. A number of test samples were prepared by diluting 5 ml of this stock solution with 5 ml of hexamine buffer at pH 6. Each test sample was extracted with 10 ml of a xylene solution of thenoyltrifluoroacetone of concentrations varying from $3 \times 10^{-2}M$ to $3 \times 10^{-1}M$, until equilibrium was reached. The activity of 5 ml of both aqueous and organic phases was measured and compared with the activity of 5 ml of the stock solution. Hence the exact amount of metal in both aqueous and organic phases was determined. The results, plotted in Fig. 6, show a slope of 2·8. This corresponds to a value of K_4 of 10^{-25}. This is in good agreement with a value of $10^{-24.8}$ calculated from available literature values of $K_1 = 10^{-6.9}$ at $2 \times 10^{-1}M$ thenyoltrifluoroacetone concentration,[8] and $K_2 = 10^{17.9}$ for the terbium–EDTA complex.[7]

Time to reach extraction equilibrium

As has been reported,[8] the rare earth metal was found to be extracted by the thenoyltrifluoroacetone very quickly. It was completely removed from the hexamine buffer at pH 6 in less than 30 sec. Similarly, after addition of a substoichiometric amount of EDTA to a rare earth metal solution the excess of metal was removed in just over 60 sec. The destruction of the metal-EDTA complex by the thenoyltrifluoroacetone took much longer to complete although equilibrium was virtually reached in a little over 60 min. For the verification experiments an extraction time of 2 hr was used.

Reproducibility

A series of test solutions was prepared by diluting 0·5–5 ml portions of a $10^{-4}M$ labelled terbium solution to 10 ml with hexamine buffer at pH 6. To each was added 1 ml of $10^{-4}M$ EDTA, this being insufficient to react with all of the metal in the more concentrated solutions. The excess of metal was extracted by adding 10 ml of $10^{-2}M$ thenyoltrifluoroacetone in xylene and shaking for 5 min. The resulting aqueous phase was filtered and a 5 ml aliquot counted. A typical plot of activity against concentration of terbium solution is shown in Fig. 7.

The sloping section of this curve indicates that the EDTA is successfully retaining the metal. Further, no metal–EDTA complex is being broken down, for if this were the case the extrapolation of this part of the curve would not rise to the equivalence point X. The flat plateau shows that when the metal is in excess a constant amount is retained in the aqueous phase. A good reproducibility curve, determined at similar concentrations to a solution to be analysed by a method based upon it, means that the analysis must be successful and give an answer correct within experimental error.

Non-reproducible conditions (*Fig.* 7). Some attempts to produce reproducibility curves show divergences from the type of curve illustrated and can be the result of one or all of three conditions:

(*i*) As the concentration of metal in the test solution decreases to the order of $10^{-6}M$ the working range of extractant concentrations becomes very small at practical pH values. The required equilibrium condition becomes increasingly difficult and finally impossible to achieve. For work at this level the K_4 values should be accurately determined under the test conditions before the range of extractant concentrations is calculated. In the rare earth series, the end members have the lowest K_4 values, and therefore the central members, are most affected.

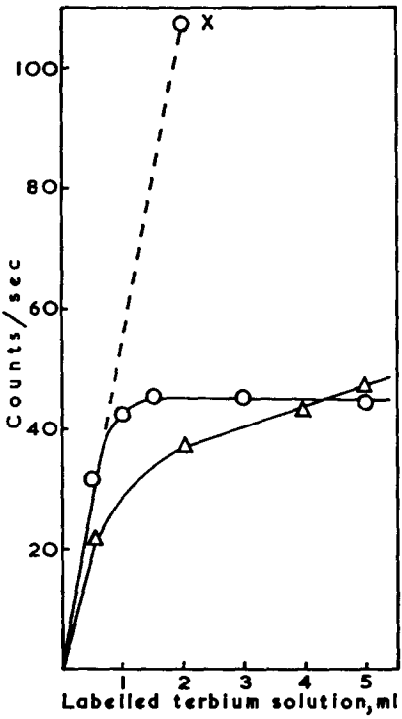

FIG. 7.—Reproducibility of extraction.
○—Reproducibility of the substoichiometric extraction of terbium in presence of EDTA.
△—Non-reproducible substoichiometric extraction of terbium in presence of EDTA.

(*ii*) The EDTA is not at all selective and foreign metal ions present in concentrations of say $10^{-7}M$ might interfere by upsetting the equilibrium. To overcome this a preliminary extraction could be used.[6]

(*iii*) The EDTA reaction may fail to reach equilibrium. We feel, however, that it is inadvisable to heat the reagents to bring the reaction to equilibrium as loss by adsorption and/or hydrolysis would give rise to even further complications. The difficulties can be partly resolved by careful choice of the degree of substoichiometry, since the value of C_{HY} [concentration of EDTA, equation (16)] rather than metal ion concentration affects the working range.

Analysis of test samples

As examples of how the technique can be used as an analytical method, a number of rare earth solutions of known concentration were analyzed by isotope dilution.

The solutions used were terbium solution labelled with ^{160}Tb, and ytterbium solution labelled with ^{170}Tm. The latter solution was readily available in our laboratory whereas radioactive isotopes of ytterbium or pure inactive thulium was not. For thulium and ytterbium the ratio of K_1/K_2 is very similar ($10^{25\cdot6}$).

To each of a number of separating funnels were added 5 ml portions of $1M$ hexamine/hexamine nitrate buffer (pH 6·0). To each were added 2 ml of a standard labelled solution, comparable in concentration to the sample. Then 2 ml of sample were transferred by pipette into some of the funnels (samples), and 2 ml of water into the rest (standards). A substoichiometric amount of EDTA (2 ml of $10^{-4}M$ EDTA for ytterbium and 1 ml of $10^{-4}M$ EDTA for terbium) was added to all the funnels, and unreacted metal was removed by shaking for 5 min with a suitable concentration of thenoyltrifluoroacetone in xylene. (The concentration is indicated by the theory and in these experiments was $10^{-2}M$.) The aqueous phases were separated and filtered, and the activity of an aliquot was measured. The amount of metal in the samples was calculated by using the substoichiometric formula

applied to isotope dilution:[1]

$$x_{\text{sample}} = x_{\text{standard}} \left(\frac{\text{activity of standard}}{\text{activity of sample}} - 1 \right)$$

where x = weight of metal. The results are shown in Table I.

TABLE I

Ytterbium			Terbium		
Taken, $\mu g/ml$	Found, $\mu g/ml$	Standard deviation, $\mu g/ml$	Taken, $\mu g/ml$	Found, $\mu g/ml$	Standard deviation, $\mu g/ml$
38·14	37·85	0·51	17·10	16·82	0·55
	38·77			17·75	
	38·46			17·42	
	38·81			17·52	
	37·85			16·87	
	38·46			16·26	
	37·33				
	37·96				
	38·66				

It must be remembered that the accuracy of the method depends on the precision of the sub-stoichiometric extraction procedure for both standard and sample. Thus the standard activity must be accurately known and should be determined as many times as possible in each set of analyses.

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Zusammenfassung—Es wird eine Theorie entwickelt, die die Gleichgewichtsbedingungen beschreibt, wenn Lösungen, die Spurenmetalle und unterstöchiometrische Mengen EDTA enthalten, mit Thenoyltrifluoraceton extrahiert werden. Zur Stützung der Theorie werden experimentelle Ergebnisse mitgeteilt. Als Anwendung wird eine Methode zur Bestimmung von Mikrogrammengen seltener Erdmetalle skizziert.

Résumé—On développe une théorie qui décrit les conditions d'équilibre lorsqu'on extrait des solutions contenant des traces de métaux et des quantités substoechiométriques d'EDTA au moyen de thénoyltrifluoracétone. On donne des preuves expérimentales à l'appui de la théorie. A titre d'application, on donne un aperçu d'une méthode pour le dosage de métaux des terres rares en quantités de l'ordre du microgramme.

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PURITY CONTROL OF URANIUM BY NEUTRON ACTIVATION ASSAY—II*

DETERMINATION OF MANGANESE, NICKEL AND COPPER

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Summary—Activation analysis is applied for the simultaneous determination of manganese, nickel and copper in different uranium samples, including metallic uranium, uranium concentrates, oxide, acetate, nitrate and sodium uranate. The analytical scheme developed is based on separation of the uranium by paper chromatography and subsequent determination of these elements in the pile-irradiated residues by simple radiochemical operations. The reliability of the scheme proposed is tested, and the limits of sensitivity of the methods worked out are ascertained. Accordingly, microgram concentrations of the elements studied could be assayed in limited quantities of the samples analysed with a precision of ±15%. Reagent-blank determinations are also considered.

NEUTRON-ACTIVATION analysis has been recently used to assay a number of trace impurities in uranium metal, concentrates and other uranium compounds of different purity grades.[1–4] This technique, however, has not commonly been used for uranium analysis, owing to the high level of radioactivity caused by fission-product radionuclides and ^{239}Np formed in irradiated samples, compared to that induced from the impurities.

The possible methods for determination of foreign elements in uranium by nuclear activation are: (*i*) activation of uranium followed by efficient decontamination and identification of the radionuclides formed,[1,2] (*ii*) the separation of the impurities from uranium and their subsequent determination by classical radiochemical methods,[3] (*iii*) the separation of uranium from its impurities and their subsequent determination radiochemically without the use of several successive decontamination cycles.[4] Each method has its limitations.

In a previous paper, it was initially planned to assay the elements of atomic number 24–30 in different uranium-containing samples.[1] A scheme was developed for simultaneous determination of chromium, iron, cobalt and zinc, based on activation of uranium and radiometric assay of ^{51}Cr, ^{59}Fe, ^{60}Co and ^{65}Zn by γ-scintillation spectrometry. However, because of the comparatively short half-lives of the radioisotopes ^{56}Mn, ^{65}Ni and ^{64}Cu, the determination of manganese, nickel and copper could not be achieved by the same scheme (*cf.* Table 1). In the present paper, analytical methods are worked out for the determination of these elements simultaneously after the separation of uranium before activation.

EXPERIMENTAL

Chemicals and samples analysed

The uranium samples analysed include: (*i*) two uranium concentrates, SP-1 and SP-2, each containing about 75% of triuranium octaoxide, both provided by "Junta de Energia Nuclear, Spain"; (*ii*) a uranium trioxide sample, H-632 from "Akteibolaget Atomenergie, Sweden"; (*iii*) a sample of metallic uranium foil, 0·16 mm thick, from USSR; (*iv*) a uranyl acetate sample from Fisher Scientific

* Part I—*Talanta*, 1966, **13**, 381.

Company, New York, with certified analysis for laboratory use; (*v*) a uranyl nitrate sample of not less than 99% purity, from May & Baker Ltd., England, and (*vi*) a sample of sodium uranate of technical purity grade, from Carlo and Erba Company, Italy.

Standards, carriers, hold-back carriers, scavengers and all other chemicals used are of analytical reagent grade.

Preparation of samples and standards

Uranium is first separated by paper chromatography.[5] Suitable weights of the samples to be analysed (250 mg) are dissolved in 5 ml of nitric acid solution (1 + 1) and the excess of acid is carefully evaporated. The residual concentrate is brought to a known volume and aliquots (200–500 μl containing about 50 mg of the sample concerned) are spotted on a strip of chromatographic paper (5 × 30 cm) and dried.

For separation of uranium, the chromatograms are developed with an acid mixture of diethyl ether and concentrated nitric acid (95:5) in an atmosphere previously equilibrated with the vapours of this mixture.[5] Uranium is completely separated in 5–7 hr, leaving the manganese, nickel and copper at the starting position. Each chromatogram is then dried and a 3-cm square with the start line in the middle is cut out and separately wrapped in thin aluminium foil and made ready for the pile irradiation.

Monitoring standards are made from suitable aliquots of standard solutions of manganese, nickel and copper in dilute nitric acid, by similar treatment. Blank chromatograms are run simultaneously under the same conditions.

Pile irradiations

Duplicate samples and standards and triplicate blanks are packed in a single irradiation can of standard type, and irradiated for 10–15 min with a mean flux 5×10^{11} n/cm^2/sec.

Processing of irradiated samples

For convenience, the shorter-lived manganese (^{56}Mn, $t_{1/2}$ 2·6 hr) and nickel (^{65}Ni, $t_{1/2}$ 2·6 hr) are separated and decontaminated before the copper (^{64}Cu, $t_{1/2}$ 12·8 hr). The squares of paper are removed from the aluminium foils and separately digested with concentrated nitric acid (5 ml) added in portions, and the solutions are carefully boiled to expel any volatile radioactive substances present. Carriers of manganese, nickel and copper (20 mg each) and hold-back carriers of iron, cobalt and zinc (5 mg each) are added to the clear solution. Nitrates are then destroyed by gradual addition of concentrated hydrochloric acid and boiling. The concentrated chloride solutions are made 1*M* in hydrochloric acid and the warm solution is treated with purified hydrogen sulphide, whereby copper sulphide is separated, and reserved for the determination of copper. The filtrate is freed from excess of hydrogen sulphide and made alkaline with filtered ammonia solution (1 + 1) and the precipitate is discarded.

The solution containing nickel, manganese and the other hold-back carriers is treated with ammonium sulphide solution and the sulphides separated are washed with warm dilute hydrochloric acid and are reserved for the nickel determination; manganese is determined in the solution.

Manganese

The solution containing manganese is made acidic with hydrochloric acid, iron carrier is added (5 mg of Fe) and the solution is made ammoniacal. The precipitate is discarded and the filtrate is acidified with concentrated nitric acid, treated with excess of fuming nitric acid (s.g. 1·42) together with a few crystals of potassium chlorate, and boiled. The hydrated manganese dioxide that separates is washed and then dissolved with a few drops of concentrated nitric acid and 30% hydrogen peroxide. Iron carrier is added to the clear solution and manganese is reprecipitated after removal of iron(III) hydroxide and made ready for activity measurement and chemical yield determination.

Nickel

The nickel and cobalt sulphides precipitated are dissolved in *aqua regia* (1 ml), and iron carrier is added (5 mg of Fe) and then precipitated as hydroxide with ammonia solution added in slight excess. The solution containing the nickel and cobalt is slightly acidified with acetic acid and then 2 ml of 1% alcoholic dimethylglyoxime solution are added. The nickel dimethylglyoximate is washed and then dissolved in concentrated hydrochloric acid and the solution is boiled. Iron carrier is added to the solution and the decontamination steps are repeated before final separation of nickel as the dimethylglyoximate.

Copper

The copper sulphide is dissolved in a minimum of boiling concentrated nitric acid. Iron carrier is added (5 mg), and the solution is made alkaline with excess of ammonia solution (1 + 1). The

precipitate is discarded and the filtrate is acidified with dilute hydrochloric acid and reduced with 10% sodium sulphite solution and the copper is then precipitated as copper(I) thiocyanate with 10% potassium thiocyanate solution. The precipitate is dissolved in concentrated nitric acid, and the copper thiocyanate is reprecipitated to free it from other activities, washed, dried, weighed and the ^{64}Cu activity is measured.

The blanks and standards treated in the same way as the samples.

Calibration

For testing the reliability of the successive operations aliquots from standard solutions of manganese, nickel and copper are spotted on paper chromatograms previously loaded with 20-mg portions of triuranium octaoxide (Johnson and Matthey "specpure") in dilute nitric acid solution. Uranium is of triuranium octaoxide (Johnson and Matthey specpure) in dilute nitric acid solution. Uranium is then separated as previously outlined and each of the elements added is assayed by the methods described. Reference standards and blanks are given the same activation as the test samples and are subsequently treated similarly. The chemical yield was never less than 50%.

Radiation measurements

In all cases, the sources separated from samples, standards and blanks are in the same chemical form. Activity measurements are generally carried out with a GM-counter (2–4 mg/cm^2 window thickness). Scintillation spectrometric measurements were also made with a 1·5 × 1 in. NaI(Tl) crystal photomultiplier assembly connected to a multi-channel pulse-height analyser.

RESULTS AND DISCUSSION

The nuclear characteristics of manganese, nickel and copper (*cf.* Table I) make their determination in uranium by classical radioactivation techniques impossible.

TABLE I.—NUCLEAR DATA

Atomic No.	Element	Abundance,* %	Cross-section, *barn*	Isotope formed	Half-life, *hr*	Principal radiations, *MeV*
25	Manganese	100	13·30	^{56}Mn	2·58	β^- 2·86, 1·05, 0.75 γ 0·85, 1·81
28	Nickel	1·08	1·52	^{65}Ni	2·56	β^- 2·10, 0·60, 1·01 γ 0·37, 1·12, 1·49
29	Copper	69·09	4·51	^{64}Cu	12·80	EC; β^- 0·571; β^+ 0·66 γ 1·34

* The values tabulated are for the stable nuclides producing the corresponding radioisotopes by (n, γ) reactions.

Other methods based on separation of uranium have been applied recently.[3,4] Systems have been developed for removal of uranium on ion-exchangers and the assessment of impurities in the eluates.[3] The expected sources of error are contamination from reagents and ion-exchangers, incomplete recovery of the impurities in the eluates, and losses due to successive handling operations before activation. Uranium has been separated on cellulose, from a number of elements with an ethereal solution containing 5% v/v of nitric acid.[5] The alkali and alkaline earth metals, rare earths, Cu, Ag, Zn, Cd, Al, In, Tl, Ti, Hf, Ge, Sn, Y, Pb, Nb, Ta, Cr, W, Te, Mn, Fe, Co and Ni remain in the start position, or move only slightly. Mercury(II), selenium, arsenic, antimony and bismuth move, but less rapidly than uranium. Separation of uranium by paper chromatography was first used by Ördögh, Szabó and Hegedüs for the determination of metallic impurities in uranium.[4] Under our experimental conditions, a simple analytical scheme is developed for the simultaneous neutron-activation determination of manganese, nickel and copper after the uranium has been separated by paper chromatography. Preliminary tests proved that diethyl ether containing 5% of nitric acid is suitable for the complete removal of uranium unaccompanied by any of the elements studied.[4,5]

The radiochemical methods described for processing irradiated samples show that possible interference due to foreign radionuclides produced from traces of uranium retained by ion-exchange on the paper, is not important. In all cases, the radiochemical purity of the radioisotopes ^{56}Mn, ^{65}Ni and ^{64}Cu was checked by following their decay (*cf.* Figs. 2, 3 and 4) and by scintillation γ-ray spectrometry.

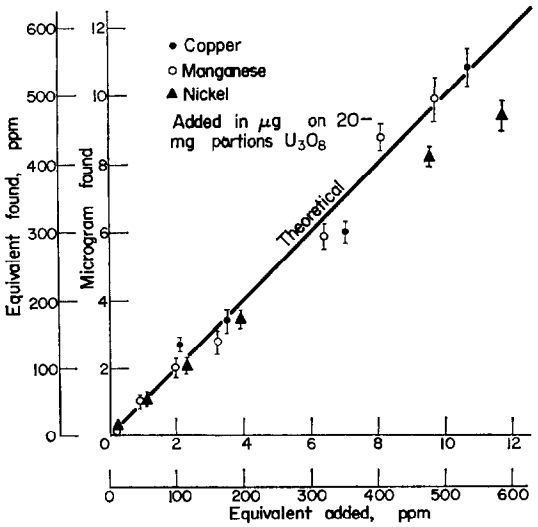

FIG. 1.—Reproducibility of neutron-activation assay.

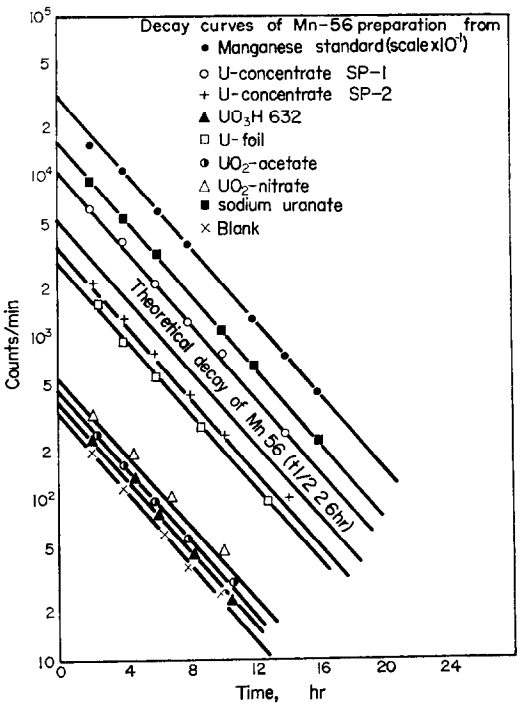

FIG. 2.—Decay curves of Mn-56.

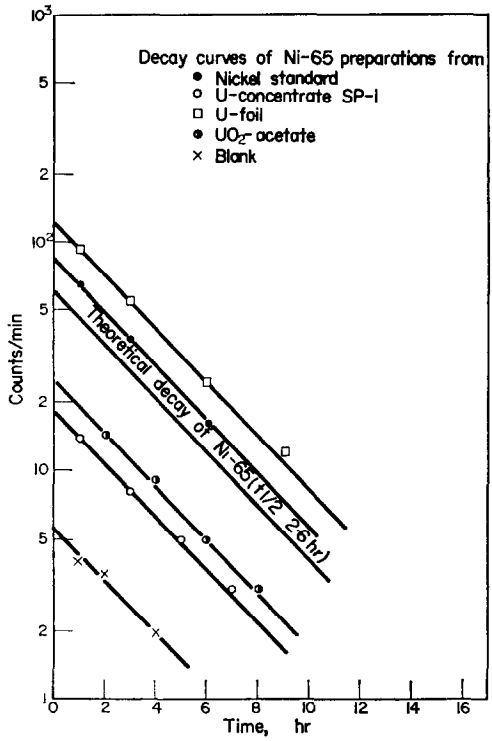

FIG. 3.—Decay curves of Ni-65.

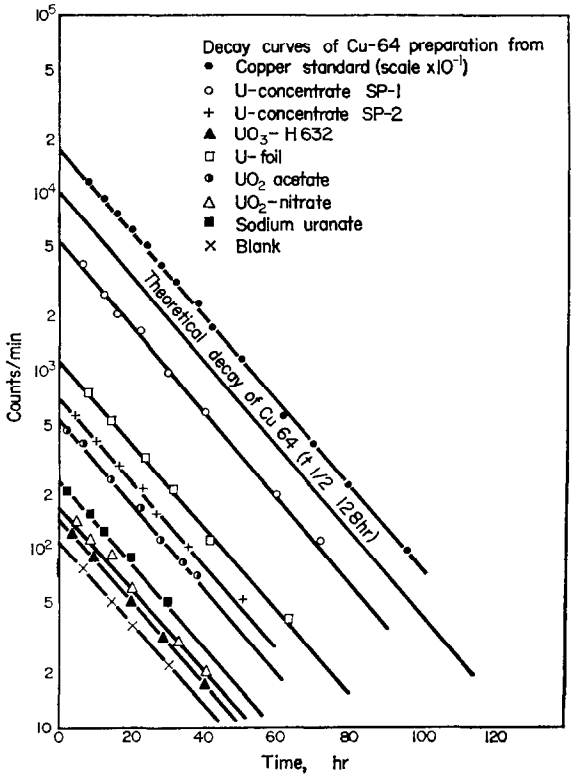

FIG. 4.—Decay curves of Cu-64.

The results of the determinations carried out are summarized in Table II. From the data reported in Table III (*cf.* Fig. 1), and from the irradiation conditions used it appears that microgram quantities of these elements can be assayed with a precision of $\pm 15\%$. The order of sensitivity attainable is that expected,[7] but it could be increased by longer irradiation at a slightly higher neutron flux.

TABLE II.—DETERMINATION OF MANGANESE, NICKEL AND COPPER IN URANIUM BY NEUTRON ACTIVATION ANALYSIS

Sample	Weight, *mg*	Elements determined, *ppm*		
		Manganese	Nickel	Copper
Concentrate SP-1	45·2	108	4·2	109
	45·2	154	29	—
	28·6	—	—	96
		131	16	102
Concentrate SP-2	35·99	31	b.d*	77
	35·99	27	b.d	74
		29	b.d	75
Uranium trioxide, H632	379·0	1·5	b.d	9
	379·0	—	b.d	9
	34·5	1·2	b.d	13
		1·3	b.d	10
Uranium foil	40·6	25	148	67
	40·6	22	184	29
	40·6	21	101	63
		23	144	53
Uranyl acetate	57·1	11	43	46
	57·1	6	19	35
		9	31	40
Uranyl nitrate	71·8	24	b.d	22
	71·8	17	b.d	19
		20	b.d	20
Sodium uranate	34·1	212	—	246
	34·1	244	—	477
	34·1	—	—	272
		228		332

* b.d represents concentrations below the limits of detection under the experimental conditions used.

TABLE III.—THE SENSITIVITY OF NEUTRON-ACTIVATION ASSAY OF MANGANESE, NICKEL AND COPPER IN URANIUM

	Taken,* *μg*			Found, *μg*		
	Mn	Ni	Cu	Mn	Ni	Cu
	0·097	0·117	0·105	b.d	0·07	b.d
	0·194	0·235	0·212	0·06	0·31	0·18
	0·970	1·177	1·057	1·05	1·34	1·08
	1·942	2·354	2·115	2·04	2·07	2·77
	3·236	3·920	3·525	2·80	3·39	3·40
	6·470	7·840	7·050	5·92	—	6·53
	9·080	9·800	8·812	8·80	8·20	6·27
	9·708	11·770	10·750	9·91	9·40	10·93
Mean error,† %				7	15	12

* Added to 20 mg of U_3O_8.
† The first two results are excluded.

Interference due to nuclear reactions involving certain elements with atomic numbers close to those of manganese, nickel and copper was also studied, especially the formation of ^{56}Mn, ^{65}Ni and ^{64}Cu by (n, p) and/or (n, α) reactions on iron, cobalt, copper and zinc. However, nuclear data[8] for the effective cross-sections and threshold energies for these reactions show that under the irradiation conditions used possible interference should be negligible.

Zusammenfassung—Mangan, Nickel und Kupfer werden in verschiedenen Uranproben, metallischem Uran, Urankonzentraten, Oxid, Acetat, Nitrat und Natriumuranat gleichzeitig aktivierungsanalytisch bestimmt. Der analytische Vorgang beruht auf papierchromatographischer Abtrennung des Urans und nachfolgender Bestimmung der genannten Elemente in den im Reaktor bestrahlten Rückständen mit einfachen radiochemischen Operationen. Die Verläßlichkeit des vorgeschlagenen Verfahrens wird geprüft und die Empfindlichkeitsgrenzen der ausgearbeiteten Vorschriften festgestellt. Demnach ließen sich Mikrogrammengen der untersuchten Elemente in begrenzten Probemengen mit einer Genauigkeit von $\pm 15\%$ bestimmen. Auch Blindbestimmungen werden besprochen.

Résumé—On applique l'analyse par activation au dosage simultané du manganèse, du nickel et du cuivre dans différents échantillons d'uranium, y compris l'uranium métallique, les concentrés d'uranium, l'oxyde, l'acétate, le nitrate et l'uranate de sodium. Le schéma analytique est basé sur la séparation de l'uranium par chromatographie sur papier et dosage subséquent de ces éléments dans les résidus irradiés à la pile par de simples opérations radiochimiques. On a essayé l'exactitude de schéma proposé, et fixe les limites de sensibilité des méthodes élaborées. En conséquence, des concentrations à l'échelle du microgramme des éléments étudiés ont pu être déterminées dans des quantités limitées des échantillons analysés avec une précision de $\pm 15\%$. On considére aussi les déterminations du témoin des réactifs.

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CATION-EXCHANGE BEHAVIOUR OF SEVERAL ELEMENTS IN NITRIC ACID–ORGANIC SOLVENT MEDIA

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Summary—The cation-exchange behaviour of 19 elements towards the strongly acidic cation-exchange resin Dowex 50-X8 in media containing varying concentrations of organic solvents and aqueous nitric acid is reported. Based on the determination of the distribution coefficients of these elements in the organic solvents methanol, ethanol, n-propanol, isopropanol, methyl glycol, acetone, tetrahydrofuran and acetic acid, the conditions most suitable for their quantitative separation are indicated and discussed.

IN a previous paper[1] the cation-exchange characteristics of 20 elements in mixed aqueous–organic solvent media containing hydrochloric acid, with Dowex 50-X8 as the exchange resin have been described. The present investigations have been carried out by employing the same resin and the same organic solvents but in media containing nitric acid. Consequently the data which are presented in these two papers can readily be compared and evaluated.

While several investigations concerning the cation-exchange behaviour of numerous metal ions in pure aqueous nitric acid solutions have been carried out[2,3] no attempt has so far been made to investigate systematically the broad field of mixed aqueous–organic solvent media containing nitric acid.

The exchange behaviour of uranium and thorium on Dowex 50-X8 from mixtures consisting of aliphatic alcohols and dilute nitric acid has been investigated[4] and on the same resin uranium has been separated from many accompanying elements with a mixture of tetrahydrofuran and nitric acid, by use of the CIESE principle.[5–7]

Apart from these investigations, cation-exchange in nitric acid–organic solvent media has received no attention. In order to obtain a much more complete picture of the adsorption characteristics and separation possibilities of elements in organic solvent media, the research work presented in this paper was performed, the most frequently employed cation-exchange resin, Dowex 50, being used in mixtures of 8 organic solvents with nitric acid. For this purpose the effect of increasing the concentration of the organic solvent from 0 to 90% in solutions with a constant overall acidity of 0·6*M* nitric acid, and the effect of changing the acidity from 0·15 to 1·2*M* while keeping the concentration of organic solvent constant at 90%, were investigated by measuring the distribution coefficients in these media. From the distribution coefficients thus obtained, the possibilities of separating the elements investigated from one another are indicated and discussed.

EXPERIMENTAL

Reagents

Ion-exchange resin. The air-dried strongly acidic cation-exchanger Dowex 50-X8 (100–200 mesh, hydrogen form) was used for the batch and column experiments.

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Standard solutions. Exactly weighed amounts of Mg, Ca, Sr, U(VI), Mn(II), Co, Ni, Cu(II), Zn, Cd, Pb, Fe(III), Al, In, Bi, Th, Ce(III), V(V) and Mo(VI) as nitrates were dissolved in 6*M* or 12*M* nitric acid to give solutions containing 10 mg of the element per ml.

Solvents. The reagent-grade pure organic solvents used were methanol, ethanol, n-propanol, isopropanol, methyl glycol, acetic acid, tetrahydrofuran and acetone.

Determination of the various elements

Most of the elements investigated (in amounts exceeding *ca.* 100 μg) were determined titrimetrically with EDTA. Microgram quantities of the metal ions were determined spectrophotometrically[8] except for uranium which was determined fluorometrically.[9]

Determination of distribution coefficients

The weight distribution coefficients of most elements, defined by the well known equation

$$K_d = \frac{\mu g \text{ of element/g of resin}}{\mu g \text{ of element/ml of solution}}$$

(see previous paper[1]), were determined by using the batch equilibrium method. Each equilibrium experiment was performed with 20 ml of a mixture consisting of 0–90% of the organic solvent, 10% of nitric acid, and water up to 100%, and containing 10 mg of the element in question. To this mixture 1 g of the resin was added and the solution was agitated on a shaking machine for 12 hr, then the resin was filtered off and the element determined in the filtrate. The experimental errors of the measurements of the distribution coefficients were virtually the same as those earlier observed in hydrochloric acid media of comparable composition.[1]

Distribution coefficients considerably smaller than 100 were determined by the column method.[10] In this case the distribution coefficient K_d was calculated from the relationship developed by Mayer and Tompkins,[11]

$$\bar{V} = K_d m$$

where m = mass of dry resin in the column and $\bar{V}$ = volume of eluent which has passed through the column to elute the maximum of the elution peak.

RESULTS AND DISCUSSION

In Tables I–XVII the metal ions are arranged in the same order. A general feature of the distribution data presented in these Tables is that in most cases the adsorption of a given element increases rather regularly with an increase in the percentage of the non-aqueous component of the mixtures and with a decrease of the nitric acid concentration.

Aliphatic Alcohol Media

In Tables I–IV, IX–XII, the distribution coefficients measured in nitric acid–aliphatic alcohol mixtures (methanol, ethanol, n-propanol and isopropanol) are shown.

Uranium(VI), thorium(IV) and cerium(III)

It is seen that in all cases the adsorption of uranium is less than that of thorium. With increasing concentration of the aliphatic alcohol the uranium adsorption increases while that of thorium remains virtually constant so that a separation of uranium from thorium would only be feasible at low alcohol concentrations. Cerium shows a behaviour similar to thorium. Thus cerium can be separated from uranium but not from thorium, It is to be expected that other lanthanide ions will behave very similarly to cerium.

When the concentration of nitric acid is increased, the adsorption of uranium decreases markedly while the adsorption of thorium and cerium is only slightly affected by a change in the acidity of the nitric acid–aliphatic alcohol mixtures. Nevertheless no ready separation of uranium from these two elements is possible at 0·6*M* or higher overall acidities of the mixtures because even under these conditions the distribution coefficients of uranium are relatively high.

TABLE I.—DISTRIBUTION COEFFICIENTS IN AQUEOUS METHANOLIC 0·6*M* NITRIC ACID

Ion	Methanol concentration, % 0	20	40	60	80	90
UO_2(II)	40	49	85	150	350	750
Th(IV)	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	7	7	8	9	7	4
V(V)	7	5	6	7	8	9
Fe(III)	171	175	190	265	290	$>10^3$
Al(III)	132	136	151	154	174	287
In(III)	173	280	300	380	$>10^3$	$>10^3$
Bi(III)	135	174	213	272	139	93
Mg(II)	18	23	28	35	60	287
Ca(II)	38	46	82	142	180	950
Sr(II)	68	203	250	676	$>10^3$	$>10^3$
Pb(II)	105	240	700	900	700	220
Zn(II)	46	53	77	148	335	543
Cd(II)	46	60	105	218	451	652
Cu(II)	27	35	50	77	79	121
Mn(II)	40	45	68	134	330	652
Co(II)	32	39	65	118	194	300
Ni(II)	30	48	103	156	300	486

Molybdenum(VI) and vanadium(V)

These show a very similar behaviour in all four alcohols so that they cannot readily be separated from each other. On the other hand it should be possible to separate molybdenum and vanadium from practically all other elements listed in the Tables. Such separations are however not readily performed because in these media molybdenum and vanadium are partly reduced to lower oxidation states which show distribution values which are higher by about one to two orders of magnitude than these of the sexi- and pentavalent oxidation states respectively.

TABLE II.—DISTRIBUTION COEFFICIENTS IN AQUEOUS ETHANOLIC 0·6*M* NITRIC ACID

Ion	Ethanol concentration, % 0	20	40	60	80	90
UO_2(II)	40	52	119	224	535	750
Th(IV)	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	7	8	8	9	7	5
V(V)	7	4	7	8	7	6
Fe(III)	171	213	269	414	$>10^3$	$>10^3$
Al(III)	132	148	172	210	264	980
In(III)	173	247	545	$>10^3$	$>10^3$	$>10^4$
Bi(III)	135	213	390	680	605	270
Mg(II)	18	22	34	168	400	953
Ca(II)	38	50	82	230	750	$>10^3$
Sr(II)	68	130	264	832	$>10^3$	$>10^4$
Pb(II)	105	500	800	$>10^3$	$>10^3$	$>10^3$
Zn(II)	46	59	123	294	913	$>10^3$
Cd(II)	46	57	98	293	465	700
Cu(II)	27	42	70	152	334	452
Mn(II)	40	53	97	245	490	$>10^3$
Co(II)	32	39	95	211	664	$>10^3$
Ni(II)	30	48	94	231	751	$>10^3$

TABLE III.—DISTRIBUTION COEFFICIENTS IN AQUEOUS n-PROPANOLIC 0·6*M* NITRIC ACID

Ion	n-Propanol concentration, % 0	20	40	60	80	90
UO_2(II)	40	85	168	207	500	890
Th(IV)	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	7	10	12	16	10	3
V(V)	7	4	5	7	7	8
Fe(III)	171	210	251	318	737	$>10^4$
Al(III)	132	151	159	201	450	$>10^4$
In(III)	173	211	545	10^3	$>10^3$	$>10^4$
Bi(III)	135	250	389	605	600	350
Mg(II)	18	26	35	54	289	947
Ca(II)	38	46	81	180	980	$>10^3$
Sr(II)	68	118	264	645	$>10^3$	$>10^4$
Pb(II)	105	740	900	$>10^3$	$>10^3$	$>10^3$
Zn(II)	46	61	123	300	$>10^3$	$>10^4$
Cd(II)	46	61	107	242	627	$>10^3$
Cu(II)	27	42	70	130	425	$>10^3$
Mn(II)	40	56	91	197	919	$>10^3$
Co(II)	32	45	84	179	760	$>10^3$
Ni(II)	30	45	81	172	$>10^3$	$>10^3$

Iron(III), aluminium(III), indium(III) and bismuth(III)

In all media the K_d-value of iron(III) increases with an increase in the concentration of the organic component of the mixtures. The reverse is true for media which contain hydrochloric acid in place of nitric acid.[1] Consequently one can assume that iron does not form anionic complexes in nitric acid media.

A behaviour similar to iron is shown by aluminium and indium, *i.e.*, their K_d-values increase regularly with increasing alcohol concentration.

An exceptional behaviour in all aliphatic alcohol media is shown by bismuth which shows adsorption maxima at alcohol concentrations of 60 or 80%, whereafter

TABLE IV.—DISTRIBUTION COEFFICIENTS IN AQUEOUS ISOPROPANOLIC 0·6*M* NITRIC ACID

Ion	Isopropanol concentration, % 0	20	40	60	80	90
UO_2(II)	40	67	159	364	890	$>10^3$
Th(IV)	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	7	7	5	3	3	3
V(V)	7	4	5	10	6	4
Fe(III)	171	188	247	279	845	$>10^4$
Al(III)	132	134	173	190	230	$>10^3$
In(III)	173	260	545	$>10^3$	$>10^4$	$>10^4$
Bi(III)	135	236	290	664	952	650
Mg(II)	18	22	36	72	366	$>10^3$
Ca(II)	38	51	102	294	$>10^3$	$>10^4$
Sr(II)	68	128	540	$>10^4$	$>10^4$	$>10^4$
Pb(II)	105	800	900	$>10^3$	$>10^3$	$>10^3$
Zn(II)	46	60	139	608	$>10^3$	$>10^4$
Cd(II)	46	65	140	402	$>10^3$	$>10^3$
Cu(II)	27	112	175	200	620	$>10^3$
Mn(II)	40	52	92	350	$>10^3$	$>10^3$
Co(II)	32	47	81	322	$>10^3$	$>10^3$
Ni(II)	30	47	90	270	$>10^3$	$>10^4$

the distribution coefficient decreases with an increase of the amount of alcohol. This suggests anionic complex formation by bismuth at alcohol concentrations exceeding 60 or 80%. This decrease in bismuth adsorption is even more pronounced when the acidity is raised at constant concentrations of aliphatic alcohols (see Tables IX–XII). Under these conditions the distribution coefficients of iron, aluminium and indium show a rather regular decrease without reaching very low values while that of bismuth decreases considerably in the acidity region from 0·6 to 1·2*M* final nitric acid concentration. Consequently separations of bismuth from these tervalent metal ions are possible at higher acidities.

Magnesium(II), calcium(II), strontium(II) and lead(II)

When the alcohol concentration is increased the adsorption of these ions shows a marked increase. A simple separation of magnesium from calcium or of calcium from strontium is impossible because of the similarity of their distribution coefficients. Thus a fractionation of these metal ions would only be possible by means of elution chromatography. A similar adsorption behaviour is observed in the case of lead.

Zinc(II) and cadmium(II)

The adsorption behaviour of these two elements is similar to that observed in the case of calcium. Because of the small differences in the K_d-values of zinc and cadmium separations of these two metal ions cannot be affected.

Copper(II) and manganese(II)

The adsorption of copper and manganese increases as the concentration of aliphatic alcohol increases to 90%. This increase is highest in propanol and lowest in methanol media, *i.e.*, the values of the distribution coefficients increase with increasing chain length of the alcohols employed.

When the concentration of nitric acid increases (see Tables IX–XII) the adsorption of copper decreases much more strongly while that of manganese does not show such pronounced variations. A separation of copper from manganese is possible in media of higher nitric acid concentrations containing methanol or ethanol.

Cobalt(II) and nickel(II)

In virtually all cases cobalt and nickel show the same adsorption behaviour and their K_d-values increase with increasing concentration and chain length of the aliphatic alcohols. Consequently no separations of these two elements from one another can be effected in any of these alcoholic media. Similar unfavourable conditions exist when the acidity is varied (see Tables IX–XII).

Methyl Glycol Media

The results of measurements of the distribution coefficients of the various elements in nitric acid–methyl glycol media are shown in Tables V and XIII.

Uranium(VI), thorium(IV) and cerium(III)

The behaviour of these elements with increasing methyl glycol concentration is virtually the same as that observed in the nitric acid–aliphatic alcohol mixtures except for a maximum of uranium adsorption at 80% of methyl glycol. This exceptional behaviour of uranium has also been observed in methyl glycol media containing

TABLE V.—DISTRIBUTION COEFFICIENTS IN 0·6*M* NITRIC ACID IN AQUEOUS METHYL GLYCOL SOLUTION

Ion	Methyl glycol concentration, %					
	0	20	40	60	80	90
UO_2(II)	40	54	110	207	434	314
Th(IV)	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	7	6	6	7	5	4
V(V)	7	5	6	7	6	4
Fe(III)	171	175	184	323	991	$>10^4$
Al(III)	132	151	169	193	203	$>10^3$
In(III)	173	540	10^3	$>10^3$	$>10^3$	$>10^3$
Bi(III)	135	358	540	952	358	258
Mg(II)	18	23	48	60	212	$>10^3$
Ca(II)	38	52	96	160	620	$>10^3$
Sr(II)	68	166	290	832	$>10^3$	$>10^3$
Pb(II)	105	630	800	$>10^3$	$>10^3$	$>10^3$
Zn(II)	46	60	88	245	860	$>10^3$
Cd(II)	46	58	112	247	505	884
Cu(II)	27	39	66	128	271	620
Mn(II)	40	53	94	224	817	$>10^3$
Co(II)	32	52	71	171	430	$>10^3$
Ni(II)	30	50	86	211	476	$>10^3$

hydrochloric acid.[1] With an increase of the acidity to 1·2*M* (see Table XIII) the distribution coefficient of uranium is considerably reduced so that this element can be separated from thorium, cerium and many other elements (the conditions of separation are, however, less suitable in this medium than in mixtures containing tetrahydrofuran or acetone (see Tables XV and XVI)).

Molybdenum(VI) and vanadium(V)

These two elements show an adsorption behaviour similar to that observed in aliphatic alcohol media and a separation of molybdenum from vanadium is impossible.

Iron(III), aluminium(III), indium(III) and bismuth(III)

As in the aliphatic alcohol media the adsorption of iron, aluminium and indium increases considerably at high methyl glycol concentrations, while that of bismuth shows a maximum at 60% of methyl glycol whereafter the distribution coefficient decreases with an increase in the concentration of this organic solvent. While the adsorption of iron, aluminium and indium is practically unaffected by variations of the nitric acid concentration, the distribution coefficient of bismuth decreases strongly with an increase in acidity. Consequently bismuth can be separated from these elements at high acidities (see Table XIII).

Magnesium(II), calcium(II), strontium(II), lead(II), zinc(II), cadmium(II), copper(II) and manganese(II)

These elements show in nitric acid–methyl glycol media a behaviour which is similar to that observed in the aliphatic alcohols. A separation of copper from the other bivalent ions would be possible at a final nitric acid concentration of 1·2*M* (see Table XIII).

TABLE VI.—DISTRIBUTION COEFFICIENTS IN 0·6*M* NITRIC ACID IN AQUEOUS ACETIC ACID

Ion	Acetic acid concentration, % 0	20	40	60	80	90
UO_2(II)	40	76	159	350	480	$>10^3$
Th(IV)	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	7	9	12	18	20	*
V(V)	7	5	7	8	7	*
Fe(III)	171	184	204	319	890	$>10^3$
Al(III)	132	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
In(III)	173	190	271	311	$>10^3$	$>10^4$
Bi(III)	135	175	270	10^3	$>10^3$	$>10^3$
Mg(II)	18	23	32	48	200	$>10^3$
Ca(II)	38	44	70	120	980	$>10^4$
Sr(II)	68	157	364	$>10^3$	$>10^3$	$>10^4$
Pb(II)	105	180	250	315	$>10^3$	$>10^3$
Zn(II)	46	53	88	192	$>10^3$	$>10^3$
Cd(II)	46	49	153	261	$>10^3$	$>10^3$
Cu(II)	27	43	70	102	380	$>10^3$
Mn(II)	40	147	258	473	$>10^3$	$>10^3$
Co(II)	32	48	75	134	560	761
Ni(II)	30	54	81	137	$>10^3$	$>10^3$

* Not determined because practically complete reduction to lower valency states occurs in these media.

Cobalt(II) and nickel(II)

In methyl glycol–nitric acid solutions cobalt and nickel show about the same behaviour as in aliphatic alcohol media and cannot be separated from each other and many other elements.

Acetone and Tetrahydrofuran Media

In Tables VII, VIII, XV and XVI are shown the results of determinations of the distribution coefficients of the various metal ions in actone and tetrahydrofuran

TABLE VII.—DISTRIBUTION COEFFICIENTS IN 0·6*M* NITRIC ACID IN AQUEOUS TETRAHYDROFURAN

Ion	Tetrahydrofuran concentration, % 0	20	40	60	80	90
UO_2(II)	40	96	134	243	51	40
Th(IV)	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
Mo(VI)	7	7	5	2	3	4
V(V)	7	7	6	5	3	4
Fe(III)	171	200	287	550	$>10^3$	$>10^3$
Al(III)	132	137	258	479	878	$>10^3$
In(III)	173	235	630	$>10^3$	$>10^3$	$>10^3$
Bi(III)	135	280	630	592	195	47
Mg(II)	18	21	36	72	357	$>14^3$
Ca(II)	38	50	102	145	760	$>14^3$
Sr(II)	68	109	228	676	$>10^3$	$>10^3$
Pb(II)	105	185	463	934	$>10^3$	$>10^3$
Zn(II)	46	58	157	704	$>10^3$	$>10^4$
Cd(II)	46	49	178	10^3	10^4	$>10^4$
Cu(II)	27	38	66	163	514	$>10^3$
Mn(II)	40	61	130	405	$>10^3$	$>10^3$
Co(II)	32	42	119	306	$>10^3$	$>10^3$
Ni(II)	30	40	115	316	$>10^3$	$>10^3$

TABLE VIII.—DISTRIBUTION COEFFICIENTS IN 0·6*M* NITRIC ACID IN AQUEOUS ACETONE

Ion	Acetone concentration, %					
	0	20	40	60	80	90
UO_2(II)	40	85	127	364	207	141
Th(IV)	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>14^4$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	7	7	5	3	2	1
V(V)	7	4	5	7	5	2
Fe(III)	171	227	256	607	$>10^4$	$>10^4$
Al(III)	132	52	84	168	573	$>10^4$
In(III)	173	322	729	$>10^3$	$>10^4$	$>10^4$
Bi(III)	135	272	605	672	125	86
Mg(II)	18	25	33	87	612	$>10^3$
Ca(II)	38	60	118	300	$>10^3$	$>10^3$
Sr(II)	68	120	390	$>10^3$	$>10^3$	$>10^3$
Pb(II)	105	850	900	$>10^3$	$>10^3$	$>10^3$
Zn(II)	46	64	120	430	$>10^3$	$>10^4$
Cd(II)	46	85	148	570	$>10^4$	$>10^4$
Cu(II)	27	44	83	237	830	$>10^3$
Mn(II)	40	61	139	387	$>10^3$	$>10^4$
Co(II)	32	58	132	395	$>10^3$	$>10^4$
Ni(II)	30	42	108	395	$>10^3$	$>10^4$

media containing nitric acid. The elements show a similar behaviour in both organic solvents especially at high nitric acid concentrations.

Uranium(VI), thorium(IV) and cerium(III)

Thorium and cerium show the same behaviour as in the organic solvent media discussed before. An exceptional behaviour is shown by uranium. Its adsorption reaches a maximum at 60% of organic solvent in both tetrahydrofuran and acetone,

TABLE IX.—DISTRIBUTION COEFFICIENTS IN 90% METHANOL MIXTURES CONTAINING 10% OF NITRIC ACID OF VARIED MOLARITY

Ion	Final HNO_3 concentration, *M*				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	$>10^3$	10^3	750	230	206
Th(IV)	$>10^4$	$>10^4$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	30	15	4	7	9
V(V)	10	9	9	8	7
Fe(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	600
Al(III)	$>10^3$	10^3	287	280	250
In(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	10^3
Bi(III)	$>10^3$	$>10^3$	93	63	22
Mg(II)	$>10^3$	10^3	287	260	200
Ca(II)	$>10^3$	$>10^3$	950	700	500
Sr(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Pb(II)	$>10^3$	$>10^3$	220	76	52
Zn(II)	$>10^3$	$>10^3$	543	390	290
Cd(II)	$>10^3$	$>10^3$	652	350	230
Cu(II)	405	246	121	91	55
Mn(II)	$>10^3$	$>10^3$	652	600	480
Co(II)	$>10^3$	$>10^3$	300	270	230
Ni(II)	$>10^3$	$>10^3$	486	265	230

TABLE X.—DISTRIBUTION COEFFICIENTS IN 90% ETHANOL MIXTURES CONTAINING 10% OF NITRIC ACID OF VARIED MOLARITY

Ion	Final HNO_3 concentration, M				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	$>10^3$	$>10^3$	750	188	130
Th(IV)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	3	5	5	5	9
V(V)	6	6	6	5	7
Fe(III)	$>10^3$	$>10^3$	$>10^3$	650	600
Al(III)	$>10^3$	$>10^3$	980	420	400
In(III)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Bi(III)	$>10^3$	$>10^3$	270	102	35
Mg(II)	$>10^3$	$>10^3$	953	900	710
Ca(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Sr(II)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Pb(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zn(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	600
Cd(II)	$>10^3$	$>10^3$	700	650	600
Cu(II)	480	462	452	210	130
Mn(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	10^3
Co(II)	$>10^3$	$>10^3$	$>10^3$	548	535
Ni(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$

whereafter the K_d-value decreases considerably. This decrease is much more pronounced in the tetrahydrofuran media (see Table VII). As a consequence uranium can be separated from virtually all elements listed in Table VII, *e.g.*, by using a medium consisting of 90% tetrahydrofuran and 10% 6*M* nitric acid. This fact has earlier been utilized for the selective analytical separation of uranium.[5] For the theoretical interpretation of this strong decrease of uranium adsorption which is even more

TABLE XI.—DISTRIBUTION COEFFICIENTS IN 90% n-PROPANOL MIXTURES CONTAINING 10% OF NITRIC ACID OF VARIED MOLARITY

Ion	Final HNO_3 concentration, M				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	$>10^3$	$>10^3$	890	172	115
Th(IV)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	20	10	3	4	6
V(V)	8	7	8	5	7
Fe(III)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Al(III)	$>10^4$	$>10^4$	$>10^4$	250	200
In(III)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Bi(III)	$>10^3$	$>10^3$	350	146	56
Mg(II)	$>10^3$	$>10^3$	947	900	890
Ca(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Sr(II)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Pb(II)	$>10^3$	$>10^3$	$>10^3$	440	60
Zn(II)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Cd(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	10^3
Cu(II)	$>10^3$	$>10^3$	$>10^3$	495	319
Mn(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Co(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ni(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$

TABLE XII.—DISTRIBUTION COEFFICIENTS IN 90% ISOPROPANOL MIXTURES CONTAINING 10% OF NITRIC ACID OF VARIED MOLARITY

Ion	Final HNO_3 concentration, M				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	$>10^3$	$>10^3$	$>10^3$	274	165
Th(IV)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	280
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	2	2	3	5	9
V(V)	5	5	4	4	4
Fe(III)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	118
Al(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
In(III)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Bi(III)	$>10^3$	$>10^3$	650	315	115
Mg(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ca(II)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Sr(II)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Pb(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zn(II)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Cd(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Cu(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	813
Mn(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Co(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ni(II)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$

pronounced at still higher acidities (see Tables XV and XVI) the CIESE-effect can be used.[5–7]

Other elements

All other elements listed in Tables VII, VIII, XV and XVI show a behaviour similar to that observed in the media discussed earlier. The K_d-value of bismuth shows a maximum at 40% of tetrahydrofuran while in acetone the maximum is at

TABLE XIII.—DISTRIBUTION COEFFICIENTS IN 90% METHYL GLYCOL MIXTURES CONTAINING 10% OF NITRIC ACID OF VARIED MOLARITY

Ion	Final HNO_3 concentration, M				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	980	750	314	126	50
Th(IV)	$>10^4$	$>10^4$	$>10^3$	10^3	225
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	6	5	4	3	3
V(V)	10	7	4	4	5
Fe(III)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Al(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
In(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Bi(III)	$>10^3$	$>10^3$	258	180	90
Mg(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	10^3
Ca(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Sr(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Pb(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zn(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Cd(II)	$>10^3$	$>10^3$	884	700	600
Cu(II)	$>10^3$	$>10^3$	620	414	180
Mn(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Co(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ni(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$

TABLE XIV.—DISTRIBUTION COEFFICIENTS IN 90% ACETIC ACID MIXTURES CONTAINING 10% OF NITRIC ACID OF VARIED MOLARITY

Ion	Final HNO_3 concentration, M				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	$>10^3$	$>10^3$	$>10^3$	434	337
Th(IV)	$>10^4$	$>10^4$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	*	*	*	*	*
V(V)	*	*	*	*	*
Fe(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Al(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
In(III)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Bi(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mg(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ca(II)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Sr(II)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Pb(II)	$>10^3$	$>10^3$	$>10^3$	560	319
Zn(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Cd(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Cu(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mn(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Co(II)	941	905	761	674	621
Ni(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$

* Not determined because practically complete reduction to lower valency states occurs in these media.

60% and in both organic solvents the adsorption decreases markedly with an increase in nitric acid concentration. For the purpose of separating molybdenum and vanadium from other elements the tetrahydrofuran mixtures are more suitable than the acetone media because in the former no reduction of these two metal ions occurs.

TABLE XV.—DISTRIBUTION COEFFICIENTS IN 90% TETRAHYDROFURAN MIXTURES CONTAINING 10% OF NITRIC ACID OF VARIED MOLARITY

Ion	Final HNO_3 concentration, M				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	$>10^3$	320	40	5	2
Th(IV)	$>10^4$	$>10^4$	$>10^3$	$>10^3$	$>10^3$
Ce(III)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Mo(VI)	2	3	4	4	3
V(V)	7	5	4	4	3
Fe(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Al(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
In(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Bi(III)	$>10^3$	$>10^3$	47	35	20
Mg(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ca(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Sr(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Pb(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zn(II)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Cd(II)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Cu(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mn(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Co(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ni(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$

TABLE XVI.—DISTRIBUTION COEFFICIENTS IN 90% ACETONE MIXTURES CONTAINING 10% OF NITRIC ACID OF VARIED MOLARITY

Ion	Final HNO_3 concentration, M				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	$>10^3$	560	141	5	3
Th(IV)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	550
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mo(VI)	3	2	1	5	10
V(V)	3	2	2	6	10
Fe(III)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Al(III)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
In(III)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Bi(III)	$>10^3$	$>10^3$	86	54	31
Mg(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ca(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Sr(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Pb(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zn(II)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Cd(II)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Cu(II)	$>10^3$	$>10^3$	$>10^3$	780	480
Mn(II)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Co(II)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Ni(II)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$

Acetic Acid Media

The results of measurements of distribution coefficients of the elements in acetic acid media containing nitric acid are shown in Tables VI and XIV. A comparison of these with those representing the systems discussed before shows that the behaviour of the elements in acetic acid is very similar to that in the aliphatic alcohols of longer chain length so that no detailed discussion need be presented.

TABLE XVII.—DISTRIBUTION COEFFICIENTS IN NITRIC ACID OF VARIED MOLARITY

Ion	Final HNO_3 concentration, M				
	0·15	0·3	0·6	0·9	1·2
UO_2(II)	396	163	40	28	18
Th(IV)	$>10^4$	$>10^4$	$>10^4$	$>10^3$	$>10^3$
Ce(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	280
Mo(VI)	11	7	7	7	4
V(V)	8	7	7	7	3
Fe(III)	$>10^3$	650	171	100	50
Al(III)	156	144	132	40	10
In(III)	$>10^3$	$>10^3$	173	140	70
Bi(III)	$>10^3$	$>10^3$	135	80	34
Mg(II)	446	120	18	15	4
Ca(II)	780	190	38	30	20
Sr(II)	$>10^3$	500	68	65	30
Pb(II)	$>10^3$	$>10^3$	105	71	32
Zn(II)	$>10^3$	300	46	25	14
Cd(II)	$>10^3$	280	46	21	16
Cu(II)	780	162	27	21	12
Mn(II)	813	207	40	30	15
Co(II)	370	165	32	22	13
Ni(II)	900	230	30	22	10

Water Media

In Table XVII the behaviour of the elements in pure aqueous solutions containing varying concentrations of nitric acid is shown. In these systems no ready separation of uranium from most elements can be effected. Also the separation of other elements would in most cases only be possible by ion-exchange chromatography.

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Zusammenfassung—Es wird über das Kationenaustauschverhalten von 19 Elementen gegen das stark saure Kationenaustauschharz Dowex 50-X8 in Medien berichtet, die wechselnde Mengen organischer Lösungsmittel und wäßrige Salpetersäure enthalten. Auf Grund der Bestimmung der Verteilungskoeffizienten dieser Elemente in den organischen Lösungsmitteln Methanol, Äthanol, n-Propanol, Isopropanol, Methylglycol, Aceton, Tetrahydrofuran und Essigsäure werden die geeignetsten Bedingungen für die quantitative Trennung der betreffenden Elemente angegeben und diskutiert.

Résumé—On décrit le comportement échangeur de cations de 19 éléments vis-à-vis de la résine échangeuse de cations fortement acide Dowex 50-X8 dans des milieux contenant des concentrations variables de solvants organiques et d'acide nitrique aqueux. En se basant sur la détermination des coefficients de partage de ces élements dans les solvants organiques méthanol, éthanol, *n*-propanol, isopropanol, méthylglycol, acétone, tétrahydrofuran et acide acétique, on indique les conditions les plus convenables à leur séparation quantitative et en discute.

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TITRIMETRIC, COULOMETRIC AND SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE FOLLOWING PERCHLORIC ACID OXIDATION IN THE PRESENCE OF PYROPHOSPHATE

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Summary—Manganese is oxidized quantitatively to a violet, tervalent pyrophosphate in a boiling mixture of equal parts of perchloric acid and phosphoric acid. This Mn(III) can be titrated potentiometrically or coulometrically with iron(II); it can also be measured spectrophotometrically. If the titrimetric method is carried out with titanium (III) or chromium(II), iron can also be titrated immediately after the manganese. The methods were applied to a new reference sample, ISU 600 Manganiferous Iron Ore, and to manganese ore, spiegeleisen, ferromanganese, and rail steel. Manganese(II) oxalate dihydrate has been reinvestigated as a primary standard and is highly recommended.

IN VIEW of the great number of methods proposed for manganese, chemists advance another method only with temerity. Perhaps, though, the very number of methods described indicates that all is not well with them, and this is borne out by an unpublished report[1] of the results of the analysis of three manganese ores by fifteen participating analysts; spreads of 0·97, 1·20 and 1·30% were found for the three ores, with about equal variations between the methods employed [persulphate, bismuthate, permanganate titration to manganese dioxide (modified Volhard), permanganate titration to manganese(III) pyrophosphate (Lingane and Karplus)] and between analysts using the same method. Whether these variations arose from deficiencies in the methods, from inhomogeneity in the samples, or from defects in the primary standards used is unsettled and we have addressed our attention to all three problems. We have developed a titrimetric and a spectrophotometric method based on the oxidation of the manganese to manganese(III) by a boiling mixture of perchloric and phosphoric acids, which in our hands has given consistent and apparently true results. We have blended a manganiferous iron ore and tested the lot for homogeneity; this material, designated ISU 600, Manganiferous Iron Ore, was prepared in sufficient amount to enable us to invite requests from others interested in a reference sample. We have re-examined the earlier primary standard, manganese(II) oxalate dihydrate,[2,3] and have found it good.

Our attention was first directed to the oxidation of manganese to manganese(III) during the development of a method of dissolving iron ore with a boiling mixture of perchloric and phosphoric acids,[4] a method which has proven highly useful for the determination of iron.[5] We have now shown that in this boiling mixture, manganese is oxidized quantitatively to manganese(III), presumably stabilized by formation of a non-dissociated pyrophosphate compound. This may then be titrated with reducing

agents or measured spectrophotometrically. The titration can be made conveniently with iron(II) sulphate or coulometrically with iron(II) ions. It may be carried out with titanium(III) sulphate or chromium(II) sulphate, with either of which iron may also be determined on the same sample by continuing the titration beyond the manganese end-point. For low manganese contents, as in steel, the spectrophotometric method offers advantages.

Titration of manganese(III) pyrophosphate is not new: Ingamells[6] titrated it with iron(II) sulphate, and used nitric acid for the oxidation; Kolthoff and Watters[7] effected the oxidation with lead dioxide and titrated with iron(II) sulphate; Heczo[8] oxidized with freshly prepared perphosphoric acid and concluded the determination iodometrically. The present method has the advantage that the oxidizing agent and the solvent acid are one, and that the excess of oxidizing agent is removed by simple dilution. Manganese ores in higher oxidation states must be given a preliminary reduction by heating with hydrochloric acid.

The colorimetric determination of manganese(III) pyrophosphate is also not new. It was first suggested by Tomula and Aho;[9] bromate was used as the oxidant in a sulphuric acid–pyrophosphoric acid solution. The results were erratic with relative errors as high as 25%. The system was investigated further by Purdy and Hume[10] who were unable to reproduce Tomula and Aho's spectra and finally abandoned orthophosphate, pyrophosphate and tripolyphosphate ligands in favour of a simple sulphate solution. Our own success with the method is based on maintaining a perchloric acid–phosphoric acid solution throughout the entire analysis. Reproducibility, stability and conformity to Beer's law are thus obtained. However, the intensity of the violet colour is low, the molar absorptivity being 75 (permanganate 2200), and interference from nickel, chromium and other coloured materials is serious and although we have applied the colorimetric method successfully to manganese rail steel we are less than enthusiastic about it.

EXPERIMENTAL

Apparatus and Reagents

Potentiometric titrations with titanium(III) sulphate, vanadium(II) sulphate and chromium(II) sulphate were carried out in a 250-ml beaker covered with a rubber stopper through which the electrodes and a nitrogen inlet tube were fitted. Potential measurements were made with a Model G Beckman pH meter and a platinum wire–saturated calomel electrode pair.

Solutions of titanium(III) sulphate, chromium(II) sulphate, and vanadium(II) sulphate were stored under nitrogen and over amalgamated zinc. These solutions were fed to a self-filling burette, all connections being made through glass tubing with Teflon stop-cocks.

A solution of titanium(III) sulphate was prepared by dissolving the appropriate amount of solid titanium(III) sulphate in 3–4*N* sulphuric acid, filtering through fritted glass, and reducing with and storing over amalgamated zinc.

A solution of vanadium(II) sulphate was prepared by dissolving the appropriate amount of reagent grade vanadium(IV) sulphate in 4*N* sulphuric acid and reducing with and storing over amalgamated zinc.

A solution of chromium(II) sulphate was prepared from reagent grade sodium dichromate by reduction with hydrogen peroxide in acid solution followed by further reduction with and storage over amalgamated zinc.

Electrolytic iron ignited in moist hydrogen was obtained from the G. Frederick Smith Chemical Company, Columbus, Ohio. Potassium manganicyanide, $K_3Mn(CN)_6$, was prepared as described by Ford-Smith.[14] Oxygen was removed from cylinder nitrogen by passage through vanadium(II) sulphate.[15]

Coulometric titrations were performed with a Sargent Model IV Coulometric Current Source. Platinum wire anodes and cathodes were used. End-points were detected by using a platinum wire–S.C.E. pair and a potentiometer with a lamp and scale galvanometer.

The coulometric cell consisted of a 200-ml cathode compartment separated from a 100-ml anode compartment by first an ultrafine and then a fine glass frit. The anode compartment contained a solution 1*M* in sodium sulphate and 0·01*M* in sulphuric acid. A similar solution was fed from a reservoir to the space between the frits, thus minimizing the migration of ions from the cathode and anode compartments and helping to ensure 100% current efficiency.

Spectrophotometric measurements were made with a Beckman D.U. spectrophotometer.

Reference sample, ISU 600, Manganiferous Iron Ore

Fifteen lb of a high manganese iron ore, obtained on the Cuyuna Range, Minnesota, was ground in a Micropulverizer to pass a 200-mesh sieve. The ground material was dried at 100° for several days and then mixed in a conical stainless-steel blender for 24 hr. Six specimens were taken from different parts of the batch at the time the blender was emptied. The manganese in each specimen was determined by the titrimetric method. The results, given below under *Results and Discussion* and in Table II, indicate that the inhomogeneity of the material is smaller than the error in the method of analysis.

ISU 600 is decidedly hygroscopic and should be dried before analysis.

An X-Ray powder photograph of ISU 600 by Dr. Donald L. Biggs, Department of Geology, Iowa State University, indicated the presence of quartz, hematite and manganite and the absence of pyrolucite and psilomelane. Manganite is the hydrated oxide of manganese(III), and a preliminary reduction with hydrochloric acid is necessary if the sample is analysed by the method described in this paper.

Manganese(II) oxalate dihydrate primary standard

Manganese(II) oxalate dihydrate was first proposed as a primary standard for manganese by Coltman[3] in 1924. It was further thoroughly studied by Werm.[8] We have confirmed the character and value of manganese(II) oxalate dihydrate and find it rather astonishing that it has not found universal adoption in the years since the Coltman and Werm work. It is particularly good as a primary standard for the method for manganese proposed here, for its use eliminates any standardization against a non-manganese-bearing standard and in particular circumvents the uncertainties of the permanganate-oxalate reaction.

After trying several methods of preparing manganese(II) oxalate dihydrate, Werm concluded that the preparation from potassium permanganate and oxalic acid led to the best product. His preparation was followed, although we have found that when starting with the reagent grade materials now available it is immaterial whether the materials be recrystallized.

Solid potassium permanganate was added slowly to a hot, concentrated solution of oxalic acid with stirring. The precipitated manganese(II) oxalate dihydrate was filtered off from the hot solution, washed well with water, dried for 24 hr at 55–60°, and stored in a vacuum over anhydrous magnesium perchlorate.

Manganese(II) oxalate dihydrate is unusual as a primary standard in that all three components of of the compound can be determined easily with precision and the composition of the material thus established. Werm made a study of the permanganate titration of oxalic acid and like others before him, notably McBride,[12] found that any delay in the titration, manganese(II) ion being present, caused some oxidation by air and high values for the titre of the permanganate. By carrying out the titration with dispatch and under identical conditions (dissolution in sulphuric acid, titration at 90°, delivery rate 25 ml/min), Werm obtained identical results in the standardization of permanganate with sodium oxalate and manganese(II) oxalate dihydrate. This work, of course, predates the detailed study of the permanganate-sodium oxalate standardization by Fowler and Bright.[13]

Our determination of the oxalate content of manganese(II) oxalate dihydrate was made by permanganate titration by the Fowler and Bright procedure (90% titration at 30°, remainder at 60°). The permanganate solution was also standardized at the same time against sodium oxalate and against electrolytic iron ignited in moist hydrogen. The results are shown in Table I. Assuming the sodium oxalate (NBS 40 g) to be 99·95% pure, these figures give for the oxalate content of manganese(II) oxalate dihydrate 49·16%, the theoretical value being 49·176%.

Determinations of the manganese content of manganese oxalate dihydrate by the new method gave values similarly close to the theoretical content; (*Results and Discussion* and Table II).

Recommended procedure

Of the three procedures given here, use the titrimetric or coulometric procedures for materials high in manganese such as pyrolucite, manganiferous iron ores, ferromanganese, and high manganese steels. In the titrimetric procedure titrate with iron(II) sulphate if only manganese is to be determined but with titanium(III) or chromium(II) sulphate if manganese and iron are to be titrated successively. Use the coulometric method if higher precision is desired, the necessary apparatus is available, and the

TABLE I.—COMPARATIVE STANDARDIZATION OF A PERMANGANATE SOLUTION AGAINST ELECTROLYTIC IRON, NBS SODIUM OXALATE, AND MANGANESE(II) OXALATE DIHYDRATE

Primary standard	Mean normality found*,	No. of variates	Relative standard deviation, *parts per 1000*
Electrolytic iron†	0·1200	6	2·0
Sodium oxalate,‡ NBS 40 g	0·1200	6	1·0
Manganese(II) oxalate dihydrate§	0·1202	6	1·2

* All analyses on same day.
† G. Frederick Smith Chemical Company; ignited in moist hydrogen.
‡ Dried at 120°C.
§ Dried at 60°C.

extra time required is warranted. Use the spectrophotometric method for the determination of manganese in steel or ores containing a few per cent of manganese, as an alternative to the periodate–permanganate spectrophotometric method when very small samples or excessive dilutions would be required.

Preparation of sample and oxidation of manganese. Place a sample containing about 220 mg (titrimetric method) or 40 mg (spectrophotometric method) of manganese in a 500-ml conical flask. If the sample contains oxides of manganese, pretreat the sample to reduce any higher oxidation states to manganese(II) by adding 15 ml of concentrated hydrochloric acid, heating, and evaporating to near dryness on a hot-plate. To this mixture and to materials bearing only manganese(II), add 30 ml of a mixture of 72% perchloric acid and 85% phosphoric acid (1 + 1). Heat the mixture on a hot-plate to a gentle boil so that the acid refluxes smoothly on the walls of the flask but no vapours of perchloric acid are expelled from the flask. Continue this boiling for 30 min after the first appearance of the violet colour of manganese(III). Cool, and determine the manganese by one of the following methods.

Titrimetric determination of manganese. If iron(II) sulphate is used as the titrant, carry out the titration in the flask used for the dissolution and oxidation. Dilute the mixture with about 5 ml of water and within 30 min titrate with 0·1*N* iron(II) sulphate. Determine the end-point potentiometrically or by the disappearance of the violet colour of the manganese(III) or with diphenylamine-sulphonic acid, adding the indicator just before the end-point.

For titration with titanium(III) or chromium(II) sulphate, transfer the solution of manganese(II) to a closed titration vessel, rinsing and washing the flask with concentrated phosphoric acid and then with water. Bubble a stream of oxygen-free nitrogen through the vessel to displace the air, and then titrate with 0·1*N* titrant, determining the end-point potentiometrically. The end-point occurs at a potential of about 0·57 V *vs.* S.C.E.

If iron is also to be determined add 10–15 g of sodium acetate [necessary if titanium(III) is used as titrant, but not necessary with chromium(II)] and continue the titration. The end-point occurs when the platinum electrode has a potential of about 0·1 V or less *vs.* S.C.E.

Coulometric determination of manganese. Place about 75 ml of 1*M* iron(III) sulphate in the cathode compartment of the coulometric titration cell. Add a few drops of a solution containing some manganese(III) pyrosphosphate. Titrate with iron(II) ion generated at a platinum cathode, following the titration with a platinum–S.C.E. pair to the end-point, in the neighbourhood of 0·75 V (platinum *vs.* S.C.E.). Set the potentiometer so that a small deflection of the galvanometer occurs, that is, so that the potential of the cell is not quite balanced, and keep the potentiometer at this setting throughout the subsequent titration. Transfer to the cell the solution obtained as described above (*Preparation of sample and oxidation of manganese*) and titrate until the galvanometer deflection is just that obtained in the pretitration. During the titration the potentiometer circuit should be closed only momentarily until close to the end-point, to avoid effecting any electrolysis by the indicator electrode. (The advantages of this method of end-point detection have been described by Cooke, Reilley and Furman.[11])

A second sample may now be added to the same solution and titrated.

Spectrophotometric determination of manganese. Transfer to a volumetric flask the oxidized sample solution (see *Preparation of sample and oxidation of manganese*) while it is still warm, the lower viscosity at the higher temperature making the transfer easier. Use a mixture of perchloric acid and phosphoric acid (1 + 1) for all rinsings and the final dilution. Measure the absorbance at 515 mμ against a perchloric acid and phosphoric acid mixture as a blank.

TABLE II.—DETERMINATION OF MANGANESE IN VARIOUS MATERIALS

Material	Method	Mean manganese found, %	No. of variates	Relative standard deviation, *parts per 1000*	Certificate or theoretical value, % Mn
ISU 600 Manganiferous Iron Ore	Titrimetric*	19·60	6†	0·62	
NBS 25b Manganese Ore	Titrimetric‡	58·37	5	1·7	58·35¶
NBS 66 Spiegeleisen	Titrimetric*	19·97 (73·56%Fe)	6 (6)	6·50 (3·34)	19·93¶ (73·45)¶
NBS 68 Ferromanganese	Coulometric**	80·77 80·62††	6	1·18	80·67¶
Manganese(II) oxalate dihydrate, primary standard	Titrimetric‡‡	30·70	6	1·91	30·694¶¶
	Coulometric**	30·704	6	0·349	30·694¶¶
NBS 100 Manganese Rail Steel	Spectrophotometric***	1·32	4	30	1·38

* Titration with titanium(II) sulphate standardized against manganese(II) oxalate dihydrate; end-point determined potentiometrically.
† One analysis on each of six samples taken at the conclusion of the blending operation.
‡ Titration with iron(II) sulphate standardized against ammonium hexanitratocerate; end-point determined with diphenylamine-sulphonic acid.
¶ National Bureau of Standards.
** Samples weighed on a semi-micro balance to the nearest 0·01 mg.
†† Corrected for chromium plus vanadium blank determined in the same manner as sample except that phosphoric acid was omitted; hydrochloric acid was used to reduce higher oxidation states of manganese; blank equivalent to 0·145 ± 0·001% of manganese.
‡‡ Titration with iron(II) sulphate standardized against potassium dichromate; end-point determined with diphenylaminesulphonic acid.
¶¶ Calculated with atomic weights taken from 1962 tables; *J. Am. Chem. Soc.*, 1962, **84**, 4912.
*** Blank used in reference cell; see text.

In similar fashion prepare a calibration curve. Weight accurately about 1·79 g of manganese(II) oxalate dihydrate primary standard. Dissolve and oxidize this material with the perchloric acid–phosphoric acid mixture as described above, and make the final dilution in a 100-ml volumetric flask, thus giving a solution about 0·1*M* in manganese. Transfer by pipette 10, 8, 6, 4, 2, and 1-ml portions of this solution into 100 ml volumetric flasks and dilute to volume with the perchloric acid–phosphoric acid mixture. Measure the absorbance at 515 mμ.

RESULTS AND DISCUSSION

Results of exploratory work which led to the final procedures are reported below; these furnish useful notes on the operation. The procedures finally recommended were applied to various reference samples; the results are given in Table II.

Oxidation of manganese

Manganese is oxidized rapidly and quantitatively in the boiling perchloric acid–phosphoric acid solution. The manganese(III) is stabilized by the formation of a non-dissociated pyrophosphate; for this compound Kolthoff and Watters[7] believe the formula to be $Mn(H_2P_2O_7)_3^{3-}$. Pyrophosphate is formed quickly in the boiling perchloric acid–phosphoric acid mixture and the addition of sodium pyrophosphate was found unnecessary, for it neither increased the stability of the manganese(III) nor speeded up the oxidation. Experiments indicated that the oxidation was complete but that on dilution with water, high concentrations of manganese(III) compound undergo slow decomposition with the formation of a brown precipitate. It is therefore necessary that the titration of large amounts of manganese be made without undue delay; within 30 min after transfer or dilution.

Some decomposition of perchloric acid occurs when it is boiled at atmospheric pressure, chlorine and oxygen being produced (Willard[16]). It was shown by Moore and Diehl[17] that on dilution this chlorine reacts with water to produce hypochlorous acid and that the hypochlorous acid has a deleterious effect if perchloric acid is being used for the destruction of organic matter prior to the determination of amino nitrogen (Kjeldahl method). In the present work a reducing action of hypochlorous acid on the manganese(III) was expected but none was found, possibly because the perchloric–phosphoric acid mixtures were always allowed to cool before any dilutions were made, permitting any chlorine to escape.

On being refluxed in a perchloric acid–phosphoric acid mixture, manganese(II) oxalate is decomposed, the oxalate being oxidized to carbon dioxide by the perchloric acid. All of the oxalate must be decomposed before manganese(III) is permanently formed. No difficulties were experienced with this procedure for dissolving and oxidizing manganese and oxalate.

Titrimetric determination

The manganese(III) pyrophosphate is a powerful oxidizing agent, $E^\circ \sim +1{\cdot}5$ V, and titration with iron(II) gives an excellent potential break at the end-point. The disappearance of the violet colour of the tervalent manganese compound serves for visual location of the end-point and occurs exactly at the potentiometric end-point. Diphenylaminesulphonic acid also serves well as an indicator and is best added just before the end-point.

The convenience of determining both manganese and iron on the same sample is

fair justification for the extra labour of preparing and storing titanium(III) or chromium(II) sulphate, assembling an anaerobic titration vessel, and carrying out the titration potentiometrically. The potential of the titanium(IV)–titanium(III) couple is highly pH-dependent and the titanium(III) titration of iron is only successful in a weakly acidic solution, most easily obtained in this titration by the addition of 10–15 g solid sodium acetate to the solution after the titration of the manganese(III). The titration curve is shown in Fig. 1. If chromium(II) sulphate is used as the titrant no sodium acetate is required and a greater potential break is observed at the iron end-point [450 mV as compared to 300 mV with titanium(III)].

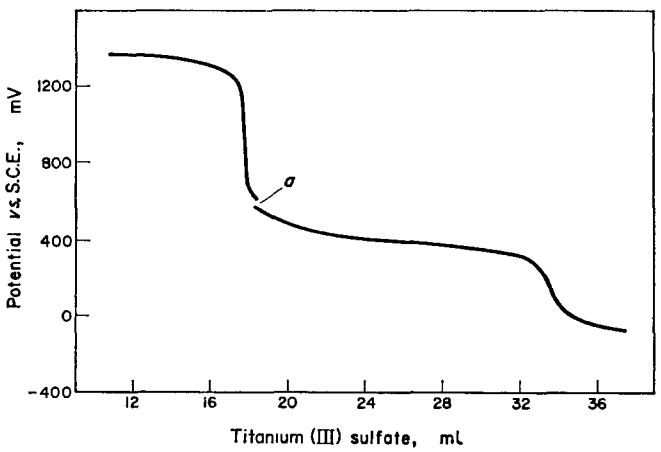

FIG. 1.—Successive potentiometric titration of Mn(III) and Fe(III) with 0·124*N* titanium(III) sulphate.
Sodium acetate, 15 g, added at point *a*.

Vanadium(II) sulphate is satisfactory as a titrant for manganese(III) but not for the subsequent titration of the iron(III). Potentials during the titration of the iron were found to be very unstable and equilibrium was not reached for several hours. Vanadium(II) is oxidized cleanly to vanadium(V) by manganese(III) and to vanadium (IV) by iron(III); the instability observed is probably caused by reaction of the vanadium(V) and iron(II) produced.

Those materials which form strong oxidizing agents when heated with boiling perchloric acid interfere in the titrimetric method, notably vanadium and chromium. This interference and a method for correcting it are discussed in a separate section below.

Coulometric titration

Its high potential makes the pyrophosphate manganese(III)–manganese(II) couple ideal for coulometric titration, and particularly convenient because the iron(III)–iron(II) couple can be used to guarantee 100% current efficiency. The potentiometric method with a platinum–S.C.E. pair proved convenient for following the reduction (Fig. 2).

Those materials which interfere in the titrimetric method interfere, of course, in the

coulometric method (see following section). In addition copper is plated on the cathode and thus also interferes, counting as manganese.

Interference of chromium and vanadium in the titrimetric and coulometric methods

Chromium and vanadium are oxidized by boiling perchloric acid to their highest oxidation states, which can then be titrated with the standard reducing agents. These oxidations are apparently complete also in the boiling mixture of perchloric and phosphoric acids, so that the proposed method for manganese gives the sum of all three metals. Correction for chromium plus vanadium can be made by a similar

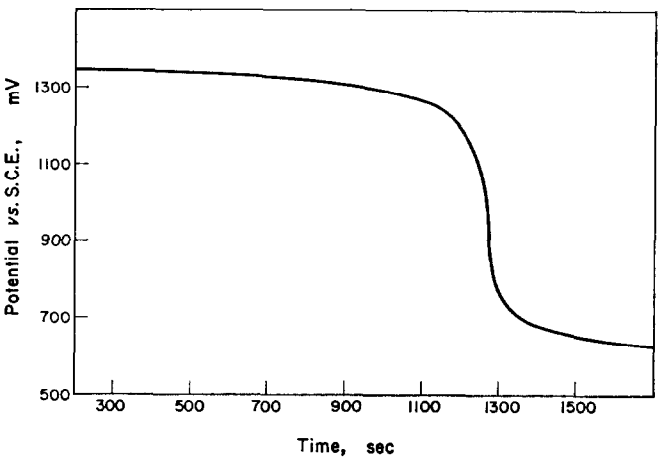

FIG. 2.—Coulometric titration of Mn(III) with electrolytically generated Fe(II). Current: 9·650 mA; 0·100 × 10^{-6} equiv/sec. Sargent Model IV coulometric current source.

determination on a separate sample with the phosphoric acid omitted. As the chromium and vanadium are low in most manganese samples, the titration should be made with 0·025*N* iron(II) sulphate, the end-point being detected conveniently with diphenylaminesulphonic acid.

The higher accuracy of the coulometric method unveiled a further source of error in the correction of the manganese determination for chromium plus vanadium just described. Any phosphorus present in the sample is converted into pyrophosphate by the boiling perchloric acid and causes corresponding small amounts of manganese to be oxidized to the manganese(III) pyrophosphate compound. Higher oxidation states of manganese, of course, are not formed in boiling perchloric acid in the absence of ligands forming non-dissociated ions. Removal of excess of permanganate in the course of a determination of chromium plus vanadium is a problem faced by earlier workers, notably Willard and co-workers, who utilized azide and also hydrochloric acid for this purpose (see Willard and Diehl[18]). Because the reduction potentials of the permanganate–manganese(II) and pyrophosphate manganese(III)–manganese(II) couples are about the same, ~ 1·5 V, it was expected that boiling with hydrochloric acid would reduce manganese(III) without reducing the chromate or vanadate, and this proved to be true.

Spectrophotometric determination

The visible spectrum of the manganese(III) pyrophosphate obtained in this work is shown in Fig. 3, and is essentially the same as that obtained by Tomula and Aho.[9] Indentical spectra were obtained by refluxing electrolytic manganese metal or manganese(II) oxalate dihydrate in the perchloric acid–phosphoric acid mixture, and by dissolving potassium manganicyanide in perchloric acid saturated with sodium pyrophosphate and warming for a few minutes. The solutions were stable for at least several weeks. The system conforms to Beer's law over the range 0·05–1 mg of manganese per ml. The molar absorptivity is low, $\varepsilon = 75.1$ cm^{-1} mole^{-1} at the wavelength of maximum absorbance, 515 mμ, and the method is therefore applicable

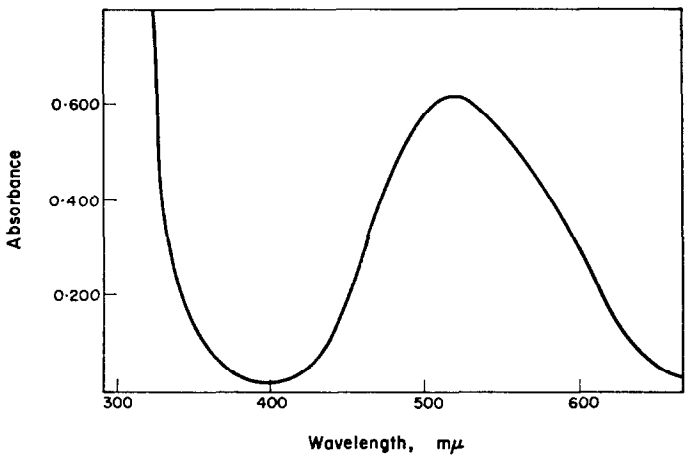

FIG. 3.—Absorption spectrum of manganese(III) in perchloric acid–phosphoric acid (1 + 1).
Manganese $8.41 \times 10^{-3}M$; 1-cm cell; absorption maximum 515 mμ; molar absorptivity 75.1 cm^{-1} mole^{-1}.

to samples of fairly high manganese content. The colours of copper, nickel, vanadium, and cobalt, which are not sufficiently intense to interfere with the permanganate colorimetric method, cause errors in the manganese(III) pyrophosphate method. Dichromate is an especially serious interference (see following section).

Interferences in the spectrophotometric method

An error of 2% in the absorbance of a sample containing 10 mg of manganese is caused by 95 mg of copper, 70 mg of nickel, or 40 mg of vanadium. Only 0·6 mg of cobalt or 0·4 mg of chromium are needed to cause the same error. These errors can be compensated by preparing a separate sample of the same material and omitting phosphoric acid during the dissolution and oxidation step, diluting to volume with a mixture of perchloric acid and phosphoric acid (1 + 1), and using this solution as the blank.

With high carbon steels, best results were obtained by dissolving the samples in 70% perchloric acid, refluxing to destroy the carbon, adding an equal volume of phosphoric acid, and continuing the refluxing to oxidize the manganese.

Results for reference samples

The accuracy and precision of the proposed methods were checked by the analysis of various reference materials; the results are summarized in Table II. These results,

of course, reflect both the precision of the method and the homogeneity of the sample. The greatest precision was obtained in the coulometric determination of the manganese in primary standard manganese(II) oxalate dihydrate, the relative standard deviation on six analyses being 0·349 parts per 1000; as the homogeneity problem is minimal with a pure material, we take this as the precision of the coulometric method. The next best precision was obtained in the titrimetric determination of manganese in ISU 600, relative standard deviation 0·62 parts per 1000. Lacking other evidence we assume this to be both the precision of the titrimetric method and evidence that the sample is blended to at least this degree of homogeneity. Poorer precision in the results for other materials may be interpreted as inhomogeneity in the sample; this was particularly noticeable in NBS 68 Ferromanganese, unless very large samples were used.

The sum of chromium and vanadium was determined in all of the reference materials analysed for manganese. This correction was made for the materials analysed by the titrimetric method by using the same procedure as for manganese but omitting the phosphoric acid. In all cases the first drop of 0·025*N* iron(II) sulphate was sufficient to bring the solution to the diphenylaminesulphonic acid end-point and the correction was thus zero. The correction became appreciable in those samples analysed by the coulometric method, owing to the increased precision and accuracy.

The analysis of the various reference materials is, of course, only as accurate as the standardizations. The standardizations of titrants used in the various analyses are listed in Table III, and in all cases show a relative standard deviation of less than 3 parts per 1000. In all cases where manganese(II) oxalate dihydrate was used as a standard an additional reference material was used to check the results, and hence the agreement of results obtained with manganese(II) oxalate dihydrate, ammonium hexanitratocerate, potassium dichromate and electrolytic iron constitutes further support for the use of manganese(II) oxalate dihydrate as a primary standard.

ISU 600 Manganiferous Iron Ore. Correction for chromium plus vanadium was negligible (titrimetric method) and we propose 19·60% manganese as a provisional value for this sample until results by others accumulate.

NBS 25b Manganese Ore. Results by the titrimetric method are in agreement with the NBS value. Correction for chromium plus vanadium was negligible although NBS reports 0·05% Cr_2O_3 (equivalent to 0·1% manganese) and 0·02% V_2O_5 (equivalent to 0·007% manganese).

NBS 66 Spiegeleisen. This material was analysed for both manganese and iron by successive titration with titanium(III) sulphate. The value obtained for manganese agrees fairly well with the NBS value but that for iron is higher than the NBS value by 0·11%. The precision for both manganese and iron was poor, far below that inherent in the method as indicated by the analysis of other materials. The results reported by the NBS collaborators range from 19·84 to 20·05% manganese. The lower precision may result from inhomogeneity in the sample or from the size of the sample, which was chosen so that both manganese and iron were determined with one loading of a 50-ml burette; the relative error in the volumes measured was thus not minimized as is possible by adjustment of the size of the sample when a single component is determined.

The correction found for chromium plus vanadium was negligible; NBS reports

TABLE III.—STANDARDIZATION OF TITRANTS USED IN ANALYSIS OF REFERENCE MATERIALS

Titrant	Primary standard	Mean normality found	No. of variates	Relative standard derivation, *parts per 1000*
Iron(II) sulphate (used in analysis of NBS 25b)	Ammonium hexanitratocerate	0·1119	6	2·3
	Manganese(II) oxalate dihydrate	0·1122	6	1·2
Iron(II) sulphate (used in analysis of manganese(II) oxalate dihydrate)	Potassium dichromate	0·02632	6	1·2
Titanium(III) sulphate (used in analysis of NBS 66 and ISU 600)	Electrolytic iron*	0·1238	6	2·8
	Manganese(II) oxalate dihydrate	0·1236	6	2·0

* G. Frederick Smith Chemical Company; ignited in moist hydrogen.

0·009% chromium and 0·012% vanadium (equivalent together to 0·04% manganese).

NBS 68 *Ferromanganese.* Results on 0·1-g samples of this material were erratic, indicating serious segregation in the sample, not at all surprising in a ferroalloy. Satisfactory results were obtained by taking suitable aliquots after dissolution of a 1-g sample and dilution to 100 ml. The determination was concluded coulometrically; the correction for chromium plus vanadium amounted to 0·15% as manganese (NBS reports 0·025% chromium, equivalent to 0·075% manganese, and 0·075% vanadium, equivalent to 0·075% manganese, total 0·150% manganese). Preliminary determinations of the correction gave values appreciably greater than expected; this was traced to the presence of phosphorus in the sample (NBS reports 0·3% phosphorus) and the formation of manganese(III) pyrophosphate. This manganese(III) was reduced by boiling with hydrochloric acid (see above under *Interference of chromium and vanadium*) in determining the correction reported in Table II.

Manganese(II) oxalate dihydrate ($MnC_2O_4.2H_2O$, *m.w.* 178·99). The manganese in the primary standard material was determined by both the titrimetric and the coulometric methods, the increased accuracy and precision obtainable by the latter being clearly evident in the results.

NBS 100 *Manganese Rail Steel.* The manganese in this sample was determined spectrophotometrically, the blank (solution in the reference cell) being a sample of NBS 100 of identical size, carried through the dissolution and oxidation operations and then manganese(III) reduced with hydrochloric acid to manganese(II) as described above. NBS reports 0·180% chromium and 0·011% vanadium in this sample.

Zusammenfassung—Mangan wird in einem siedenden Gemisch gleicher Teile Überchlorsäure und Phosphorsäure quantitativ zu einem violetten dreiwertigen Pyrophosphat oxidiert. Dieses Mangan(III) kann potentiometrisch oder coulometrisch mit Eisen(II) titriert oder spektrophotometrisch gemessen werden. Wird die Titration mit Titan(III) oder Chrom(II) ausgeführt, so kann Eisen direkt nach dem Mangan titriert werden. Die Methoden wurden auf eine neue Referenzprobe, das manganführende Eisenerz ISU 600, auf Manganerz, Spiegeleisen, Ferromangan und Schienenstahl angewandt. Mangan(II)oxalat-Dihydrat wurde als primärer Standard nachgeprüft und wird sehr empfohlen.

Résumé—On oxyde quantitativement le manganèse en un pyrophosphate trivalent violet dans un mélange bouillant d'acide perchlorique et d'acide phosphorique en parties égales. On peut titrer ce manganèse(III) par potentiométrie ou coulométrie avec le fer(II); on peut aussi le doser par spectrophotométrie. Si la méthode titrimétrique est menée avec le titane(III) ou le chrome(II), on peut aussi titrer le fer immédiatement après le manganèse. On a appliqué ces méthodes à un nouvel échantillon de référence, le minerai de fer ISU 600 manganiferreux, et au minerai de manganèse, au spiegeleisen, au ferromanganèse et à l'acier pour rail. On a réétudié l'oxalate de manganèse(II) dihydraté en tant qu'étalon primaire et le recommande fortement.

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ELEMENTS DE FLUORIMETRIE ORGANIQUE FONCTIONNELLE

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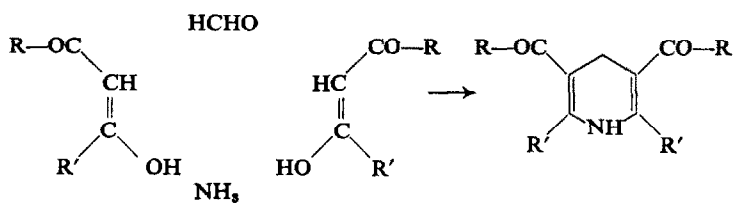
Résumé—Par des traitements chimiques convenables les 1,2-diols, hexitols, alcools primaires α-aminés, dérivés 2-nitroaliphatiques 1-hydroxylés, dérivés éthyléniques en R—CH=CH_2 et 17-cétolstéroïdes libèrent du formaldéhyde qu'on condense en un dérivé de la dihydrolutidine dosable par fluorimétrie. La formation de dérivés de la dihydropyridine autorise également la fluorimétrie des alcoylamines primaires, des nitriles et des aldéhydes aliphatiques. Les aldéhydes α-méthyléniques et les 2-désoxy oses sont dosables par cyclisation en quinaldines. Le composé fluorescent que donne l'acide glyoxylique avec le résorcinol permet d'accéder au dosage des acides α,β-dihydroxylés et hexuroniques après leur oxydation periodique. La fluorimétrie des phénols est réalisée par conversion en coumarines.

ON SAIT que l'étude spectrale des lumières incidente et émise a permis le développement de la spectrofluorimétrie au cours de ces dix dernières années. Les recherches dans ce domaine ont été nombreuses, aussi bien sur les composés à fluorescence native que sur ceux pouvant l'acquérir à l'aide d'une réaction chimique convenable. Les applications sont toutefois restées limitées, dans ce dernier cas, à des composés particuliers sans évoquer pratiquement l'extension à l'analyse fonctionnelle.

La connaissance des schémas réactionnels apparaît cependant aussi fructueuse en fluorimétrie qu'en colorimétrie. Selon nos essais, une étude théorique préalable peut permettre, en effet, par une réaction chimique portant sur la fonction à doser, d'accéder à une structure fluorescente. Par ailleurs, la fluorimétrie de composés simples, tels que le formaldéhyde ou l'acide glyoxylique, peut être étendue à des groupes fonctionnels susceptibles de les former intermédiairement. Ainsi, le choix, dans l'ensemble des possibilités réactionnelles déjà connues, apporte les différentes sélectivités dont nous faisons état dans ce premier mémoire.

La réaction de Hantzsch, par condensation du formaldéhyde sur une β-dicétone ou un ester β-cétonique en présence d'ammoniac, conduit aux dérivés substitués de la



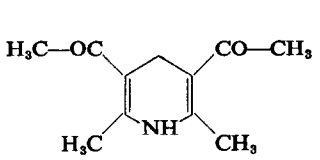
dihydropyridine. D'abord utilisée par Nash[1] et Belman[2] pour le dosage du formaldéhyde à l'aide d'acétylacétone et d'ammoniac, la cyclisation a été inversement appliquée à la colorimétrie des amines primaires aliphatiques[3] qui apportent l'azote hétérocyclique.

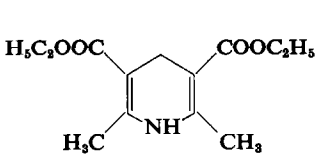
En fluorimétrie fonctionnelle, on peut retenir sur ce principe trois réactifs:

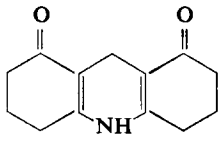
(*a*) l'acétylacétone qui, avec le formaldéhyde et l'ammoniac, forme la diacétyl-3,5 dihydro-1,4 lutidine (I), dont les solutions colorées en jaune montrent une fluorescence jaune-vert;

(*b*) l'acétylacétate d'éthyle, dont la condensation dans les mêmes conditions conduit à la dicarbéthoxy-3,5 dihydro-1,4 lutidine (II), substance aux solutions incolores mais fluorescentes en bleu:

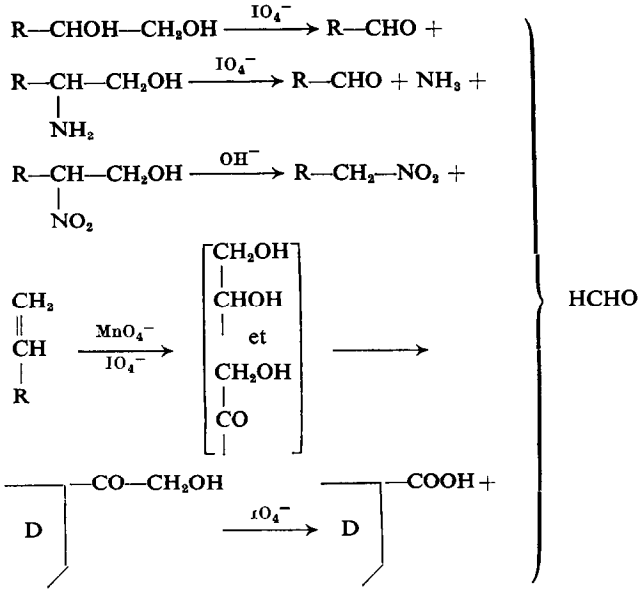
(*c*) la cyclohexane dione-1,3, qui autorise l'accès à la dioxo-1,8 décahydroacridine (III) fluorescente en bleu en milieu acide, en jaune-vert en milieu alcalin.


(I)


(II)


(III)

Plusieurs groupes fonctionnels sont susceptibles de donner naissance à du formaldéhyde par traitement convenable. Tel est le cas de l'oxydation periodique des diols-1,2, des hexitols et des alcools primaires α-aminés, de la décomposition alcaline des dérivés nitro-2 aliphatiques hydroxylés-1, de l'hydroxylation, puis de l'oxydation du glycol ou du cétol formé par action d'un réactif periodate-permanganate sur les dérivés éthyléniques en R—CH=CH_2, enfin de l'oxydation des cétol-17 stéroïdes (libres) par l'ion periodate.

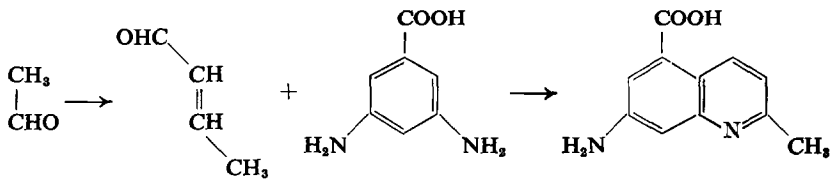


Dans ces différents cas, c'est l'acétylacétate d'éthyle que nous avons choisi comme réactif, et c'est donc la formation de la lutidine (II) qui a été mesurée.

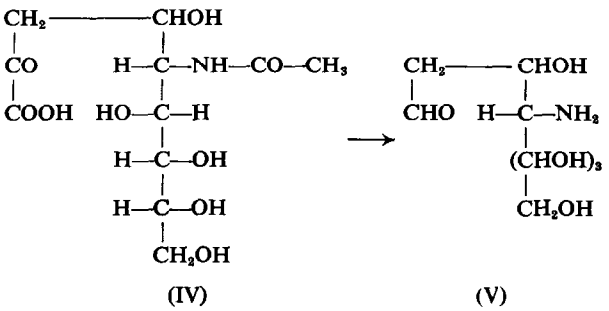
La réaction est inversement applicable à la fluorimétrie des alcoylamines primaires, avec formation de dihydrolutidines N-substituées. L'étalon alors utilisé est la lutidine (I), obtenue à partir de l'acétylacétone.

Les nitriles, qui sont aisément réduits par les hydroborures alcalins et le palladium en amines primaires,[4] bénéficient de la fluorimétrie précédente.

En remplaçant le formaldéhyde dans la réaction de Hantzsch, les aldéhydes aliphatiques peuvent aussi former des hétérocycles azotés. Le réactif de choix est dans ce cas la cyclohexane dione-1,3, et les composés fluorescents obtenus sont les alcoyl-9 dioxo-1,8 décahydroacridines. Nous rappelons ici que, par action de l'acétaldéhyde sur l'acide diamino-3,5 benzoïque, une quinaldine, la méthyl-2 carboxy-5 amino-7 quinoléine, a été isolée. Sa structure, que nous avons précisée en 1948, fait apparaître l'intervention du méthylène voisin du carbonyle, suivant le schéma de Doebner–Miller.[5]



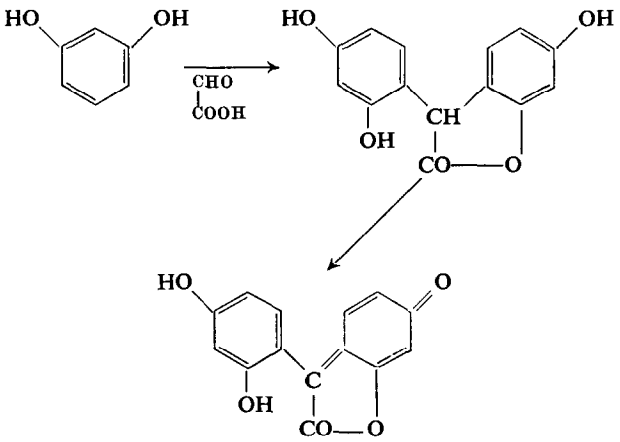
De ce fait, seuls les aldéhydes en R—CH_2—CHO sont capables de développer la fluorescence jaune-vert des amino-7 quinaldines.[6] La réaction a été appliquée au dosage du semi-aldéhyde succinique[7] ainsi qu'à celui des desoxy sucres, en particulier du désoxy-2 D-glucose[8,9] du désoxy-2D-ribose et, partant, de l'acide désoxyribonucléique.[10,11] L'acide sialique ou N-acétylneuraminique (IV) est un acide α-cétonique que l'on décarboxyle et désacétyle aisément à chaud en milieu acide en désoxy-2 amino-4 octose (V), aldéhyde en R—CH_2—CHO qui fournit alors la réaction diaminobenzoïque.[12]



(IV) (V)

Une réaction que nous avons obtenue avec le résorcinol est caractéristique de l'acide glyoxylique. Le produit de condensation s'est révélé être la lactone de l'acide tétrahydroxy-2,2',4,4' diphénylacétique, dont l'oxydation en milieu alcalin conduit à une structure quinonique fluorescente en jaune-vert. L'identification de la lactone montre que le schéma réactionnel ne peut s'appliquer qu'à l'acide aldéhydique le plus simple, l'acide glyoxylique, expliquant de ce fait la spécificité de la réaction.[13,14]

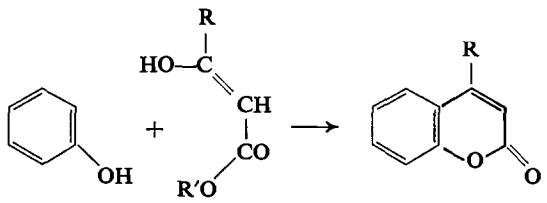
Plusieurs composés fournissent l'acide glyoxylique par une réaction chimique préalable. C'est ainsi que cet acide aldéhydique est aisément et sélectivement obtenu par réduction de l'acide oxalique à l'aide de l'amalgame d'aluminium ou du couple zinc-cuivre,[13] par deshalogénation de l'acide dichloracétique par l'hydrazine,[15] ou encore par oxydation de l'acide acétique par l'ion periodate et l'eau oxygénée.[16]



En analyse fonctionnelle, les acides α,β-dihydroxylés et en particulier les acides hexuroniques formant de l'acide glyoxylique par oxydation periodique sont aisément dosés par fluorimétrie:

$$R—CHOH—CHOH—COOH \rightarrow R—CHO + CHO—COOH.$$

Suivant le schéma de Von Pechmann-Duisberg, les esters β-cétoniques se condensent sur les phénols, en présence d'acide sulfurique, avec formation de coumarines.



La réaction est déjà classique pour le dosage de l'acétylacétate d'éthyle à l'aide du résorcinol avec formation de méthylombelliférone. Mais elle donne également accès à une fluorimétrie de l'hydroxyle phénolique, les coumarines formées étant révélées par leur fluorescence bleue.

PARTIE EXPÉRIMENTALE*

Expression de la sensibilité en fluorimétrie

Alors qu'en colorimétrie la sensibilité d'une réaction peut être définie par la quantité de substance nécessaire pour obtenir, en cuve de 1 cm d'épaisseur par exemple, une densité optique de 0,3 (50% de transmission), la réponse des fluorimètres ne conduit pas à une expression en valeur absolue. On ne peut accéder à celle-ci qu'au moyen de mesures complémentaires suivies de calculs.[17]

Pour l'analyste désirant simplement effectuer un dosage, il apparaît plus significatif de mentionner, d'une part, les limites des prises d'essai pour lesquelles l'intensité de fluorescence est linéairement proportionnelle à la concentration et, d'autre part, les prises d'essai de substance étudiée (en μg) et d'étalon (en μg/ml) pour obtenir la même réponse de l'appareil. Nous avons choisi arbitrairement les concentrations qui, dans nos conditions opératoires, correspondent à 50% de l'échelle d'étalonnage de l'appareil de mesure.

* Avec Mme C. Colombat, Mme P. Balleydier et Melle M. Pépin.

Ces données permettent le réglage, à l'aide de l'étalon d'autres fluorimètres pour obtenir, avec les prises d'essai indiquées, des mesures aisément comparables aux nôtres.

Nos lectures ont été effectuées avec le fluorimètre Electro Synthèse (France) muni de filtres interférentiels pour l'excitation et d'un monochromateur interférentiel pour l'émission. Les longueurs d'onde de la lumière excitatrice se situent ainsi à 366, 405, 436 et 546 mμ, et sont accessibles aussi bien avec les lampes à mercure qu'avec l'arc au xénon.

Il est toujours préférable d'utiliser comme étalon la substance fluorescente obtenue dans la réaction, ou tout au moins une substance dont la longueur d'onde d'émission maximale est très proche de celle de l'essai. En principe, l'excitation à longueur d'onde maximale serait souhaitable. Toutefois, pour les fluorimétries fonctionnelles, les composés formés peuvent avoir des spectres d'excitation différents. C'est en particulier le cas des condensats que donnent les aldéhydes aliphatiques avec la cyclohexane 1,3-dione. Il est dès lors préférable d'adopter pour l'excitation la longueur d'onde la plus proche du maximum du spectre de l'étalon.*

Comparée aux colorimétries usuelles,[18] la sensibilité des méthodes que nous décrivons ici apparaît 10 à 100 fois plus grande.

Préparation des étalons

Diacétyl-3,5 *dihydro*-1,4 *lutidine(I)*, *dicarbéthoxy*-3,5 *dihydro*-1,4 *lutidine(II)*, *dioxo*-1,8 *décahydroacridine(III)*. Ces composés ont été précédemment décrits.[19–21] Un mode opératoire commun a été retenu.

On dissout 3 g d'acétate d'ammonium et 1 ml de solution aqueuse à 30% de formaldéhyde dans 50 ml d'eau et ajoute 0,02 mole de β-dicétone ou d'ester β-cétonique. Après chauffage à reflux, 10 mn avec l'acétylacétone et l'acétylacétate d'éthyle, 30 mn avec la cyclohexane dione-1,3, on refroidit à 0° pendant 2 h, essore et sèche sous vide sulfurique. Les rendements sont respectivement de 62, 45 et 30%.

Les composés (I) et (II) sont recristallisés dans 20 ou 14 volumes d'éthanol avec traitement au noir. Rendements: 62 et 59%.

Le composé (III) est mis en suspension dans 12 volumes d'éthanol puis on ajoute 26 volumes de solution éthanolique *N* de potasse, traite au noir et acidifie par l'acide acétique jusqu'à virage au jaune clair de la solution orangée (environ 3 ml). Après 2 h de repos à 0°, on essore, lave avec le minimum d'éthanol et sèche sous vide sulfurique. Rendement: 64%.

On peut également recristalliser en présence de noir dans 370 volumes d'éthanol. Rendement: 61%.

Composé (I), F = 230°; composé (II), F = 192–193°; composé (III), ne fond pas à 300°.

Comparaison avec lesé talons fluorimétriques classiques: sulfate de quinine à $2H_2O$ et fluorescéine sodique:

(*a*) Diacétyl-3,5 dihydro-1,4 lutidine (I). Solution dans l'alcool aqueux à 50%. Excitation (Ex) = 436 mμ; maximum du spectre d'émission (Fl) = 510 mμ. La solution à 1 μg/ml fournit la même réponse que la solution aqueuse à 0,054 μg/ml de fluorescéine sodique.

(*b*) Dicarbéthoxy-3,5 dihydro-1,4 lutidine (II). Solution aqueuse à 1,2 ou 3% d'éthanol; Ex = 366 mμ; Fl = 470 mμ; 2 μg/ml = 0,3 μg/ml de solution de sulfate de quinine dans l'acide sulfurique 0,1*N*.

(*c*) Dioxo-1,8 décahydroacridine (III). Fluorescence bleue: solution dans l'eau contenant 2% d'éthanol; Ex = 366 mμ; Fl = 470 mμ; 0,5μg/ml $\equiv$ 1,87 μg/ml de solution de sulfate de quinine dans l'acide sulfurique 0,1*N*. Fluorescence jaune-vert: solution dans le mélange éthanol 2 ml, lessive de soude 20 ml, eau pour 100 ml; Ex = 436 mμ; Fl = 520 mμ; 1 μg/ml = 0,57 μg/ml de solution aqueuse de fluorescéine sodique.

Méthyl-2 *carboxy*-5 *amino*-7 *quinoléine*. Préparée selon Velluz *et al.*[23] Solution dans l'eau contenant 10% v/v d'acide acétique; Ex = 405 mμ; Fl = 495 mμ; 0,3 μg/ml = 3,6 μg/ml de fluorescéine sodique en solution aqueuse.

Techniques fluorimétriques

Diols-1,2 *et hexitols, alcools primaires* α-*aminés*

Principe. Oxydation periodique, puis fluorimétrie du formaldéhyde obtenu par condensation sur l'acétylacétate d'éthyle et l'ammoniac: fluorescence bleue.

Réactifs. (*a*) Solution aqueuse 0,05*N* de métaperiodate de sodium. (*b*) Solution de 2,35 g de chlorure stanneux (Cl_2Sn, $2H_2O$) dans 5 ml d'acide chlorhydrique concentré que l'on dilue à 100 ml avec de l'eau. (*c*) Solution à 4% v/v d'acétylacétate d'éthyle dans une solution aqueuse à 20 g pour 100 ml d'acétate d'ammonium.

* Déterminations effectuées avec le spectrofluorimètre Aminco-Bowman (American Instrument Co).

Mode opératoire. A 1 ml de solution aqueuse d'un dialcool, on ajoute 0,5 ml de réactif *a* et, après 30 mn de repos à température ordinaire, 0,5 ml de réactif *b* puis 2 ml d'eau et 1 ml de réactif *c*, en agitant après chaque addition. On chauffe pendant 20 mn à 60°, laisse refroidir et filtre. Lecture à l'excitation 366 mμ, émission 470 mμ.

Etalon: solution de dicarbéthoxy-3,5 dihydro-1,4 lutidine dans l'eau à 2% d'éthanol.

Applications

Voir Tableau I

TABLEAU I

	Limites du dosage, μg	Lecture 50 Essai, μg	Lecture 50 Etalon, $\mu g/ml$
Dialcools-1,2			
Glycol	1–5	2,0	1,95
Propylèneglycol	1–10	4,3	1,75
Glycérol	1–5	2,1	1,54
Dihydrostreptomycine (sulfate)	20–100	42,0	1,61
Hexitols			
Mannitol	5–25	10,0	2,63
Sorbitol	3–15	6,0	1,82
Alcools primaires α-aminés			
Monoéthanolamine	1–5	2,0	2,0
Sérine	4–20	9,0	2,23

Dérivés nitro-2 aliphatiques hydroxylés-1

Principe. Décomposition en milieu alcalin en nitroalcane et formaldéhyde que l'on condense sur l'acétylacétate d'éthyle en présence d'ammoniac: fluorescence bleue.

Réactif. Solution à 2% v/v d'acétylacétate d'éthyle dans une solution aqueuse à 20 g pour 100 ml d'acétate d'ammonium.

Mode opératoire. A 1 ml de solution aqueuse de dérivé nitro-hydroxylé, on ajoute 1 ml de solution de soude 0,5*N* puis, après 5 mn de repos à température ordinaire, 1 ml d'acide chlorhydrique *N* et 1 ml de réactif. On chauffe à 60° pendant 20 mn et refroidit à température ordinaire dans un bain d'eau-glace. Lecture à l'excitation 366 mμ, émission 470 mμ.

Etalon: solution de dicarbéthoxy-3,5 dihydro-1,4 lutidine dans l'eau à 1% d'éthanol.

Applications

Voir Tableau II.

TABLEAU II

	Limites du dosage, μg	Lecture 50 Essai, μg	Lecture 50 Etalon, $\mu g/ml$
Nitro-2 butanol-1	2–10	4	0,94
Nitro-2 méthyl-2 propanediol-1,3	1–5	2,1	1,09
Nitro-2 éthyl-2 propanediol-1,3	1–5	2,2	1,07

Dérivés éthyléniques en R—CH=CH_2

Principe. Par action d'un réactif periodate-permanganate, hydroxylation puis oxydation en formaldéhyde dosé comme précédemment: fluorescence bleue.

Réactifs. (*a*) Solution aqueuse 0,05*N* de métaperiodate de sodium. (*b*) Solution aqueuse 0,005*N* de permanganate de potassium. (*c*) Solution 0,1*N* d'arsénite de potassium (anhydride arsénieux, 4,945 g; solution *N* de potasse, 75 ml; bicarbonate de potassium, 40 g; eau, q.s.p. 1000 ml). (*d*) Solution à 2% v/v d'acétylacétate d'éthyle dans une solution aqueuse à 20 g pour 100 ml d'acétate d'ammonium.

Mode opératoire. A 1 ml de solution pyridinique de dérivé éthylénique, on ajoute 4 ml d'eau, 1 ml de réactif *a* et 1 ml de réactif *b*. Après 30 mn de repos à température ordinaire, on introduit 2 ml de réactif *c*, mélange et ajoute 2 ml de réactif *d*. On chauffe pendant 20 mn à 60° puis refroidit à température ordinaire dans un bain d'eau-glace. Lecture à l'excitation 366 mμ, émission 470 mμ.

Etalon: solution de dicarbéthoxy-3,5 dihydro-1,4 lutidine dans l'eau à 3% v/v d'éthanol.

Applications

Voir Tableau III.

TABLEAU III

	Limites du dosage, μg	Lecture 50 Essai, μg	Etalon, $\mu g/ml$
Alcool allylique	2–10	3,5	2,24
Styrolène	4–20	7,2	2,55
Quinine	10–50	16,0	1,97

Cétol-17 stérotdes

Principe. Oxydation periodique du cétol; le formaldéhyde est ici encore révélé par l'acétylacétate d'éthyle en présence d'ammoniac: fluorescence bleue.

Réactifs. (*a*) Solution aqueuse 0,01*M* de métaperiodate de sodium. (*b*) Solution de 0,25 g de chlorure stanneux ($Cl_2Sn, 2H_2O$) dans 100 ml d'acide chlorhydrique *N*, préparée extemporanément. (*c*) Solution à 4% v/v d'acétylacétate d'éthyle dans une solution aqueuse à 20 g pour 100 ml d'acétate d'ammonium.

Mode opératoire. A 1 ml de solution d'un cétol dans l'eau à 2% d'éthanol, on ajoute 0,2 ml de réactif *a* puis, après 20 mn de repos à température ordinaire, 0,8 ml de réactif *b*, 0,8 ml de soude *N* et 1,2 ml d'eau dans l'ordre indiqué. Après addition de 1 ml de réactif *c*, on chauffe pendant 20 mn à 60°, laisse refroidir et filtre. Lecture à l'excitation 366 mμ, émission 470 mμ.

Etalon: solution de dicarbéthoxy-3,5 dihydro-1,4 lutidine dans l'eau à 2% d'éthanol.

Applications

Voir Tableau IV.

TABLEAU IV

	Limites du dosage, μg	Lecture 50 Essai, μg	Etalon, $\mu g/ml$
Désoxycorticostérone	6–30	12,0	1,75
Cortisone	6–30	12,0	1,85
Prednisone	6–30	12,0	1,85
Prednisolone	8–40	17,0	2,05

Alcoylamines primaires

Principe. Formation de dihydrolutidines N-substituées par condensation sur l'acétylacétone et le formaldéhyde: fluorescence jaune-vert.

Réactif. A 10 ml de solution aqueuse *M* d'acétate de sodium, on ajoute extemporanément 0,8 ml d'acétylacétone et 2 ml de solution aqueuse à 30% de formaldéhyde. On dilue à 30 ml par l'eau.

Mode opératoire. A 2 ml de solution aqueuse sensiblement neutre d'amine, on ajoute 2 ml de réactif, bouche les tubes par un tampon de coton, chauffe pendant 10 mn au bain-marie bouillant à l'abri de la lumière vive et laisse refroidir à température ordinaire. Lecture à l'excitation 436 mμ émission 510 mμ.

Etalon: solution de diacétyl-3,5 dihydro-1,4 lutidine dans l'alcool à 50% v/v.

Applications

Voir Tableau V.

TABLEAU V

	Limites du dosage, μg	Lecture 50 Essai, μg	Lecture 50 Etalon, $\mu g/ml$
Ethylamine (chlorhydrate)	2,5–10	3,3	1,0
n-Propylamine	1–5	2,0	1,1
n-Butylamine	1–5	1,9	1,0
Benzylamine	1–5	2,2	1,65

Nitriles

Principe. Réduction par l'hydroborure de potassium, en milieu alcalin en présence d'un sel de palladium, avec formation d'amine primaire. Condensation comme ci-dessus.

Réactifs. (*a*) Solution à 0,2% d'hydroborure de potassium dans la soude *N*. (*b*) A 10 ml de solution aqueuse *M* d'acétate de sodium, on ajoute extemporanément 0,8 ml d'acétylacétone et 2 ml de solution aqueuse à 30% de formaldéhyde. On dilue à 30 ml par la solution aqueuse *M* d'acétate de sodium.

Mode opératoire. Dans 1 ml de solution hydroalcoolique de nitrile, on introduit 1 ml de réactif *a* et 0,05 ml de solution aqueuse à 0,5% de chlorure de palladium. Après 10 mn de repos à température ordinaire, acidification par 1 ml d'acide chlorhydrique 2*N* et agitation, cessation de dégagement gazeux, on ajoute 2 ml de solution aqueuse *M* d'acétate de sodium et 2 ml de réactif *b*. On chauffe pendant 10 mn au bain-marie bouillant, laisse refroidir et filtre. Lecture à l'excitation 405 mμ, émission 490 mμ.

Etalon: solution alcoolique de diacétyl-3,5 dihydro-1,4 lutidine.

Applications

Voir Tableau VI

TABLEAU VI

	Limites du dosage, μg	Lecture 50 Essai, μg	Lecture 50 Etalon, $\mu g/ml$
Benzonitrile	2–10	4,0	3,12
Cyanure de benzyle	3–15	6,0	3,03

La technique ne donne pas de bons résultats avec les nitriles qui, par réduction, conduisent à des amines relativement volatiles, comme par exemple l'acétonitrile.

Aldéhydes aliphatiques

Principe. Par action de la cyclohexane dione-1,3 en présence d'ammoniac, formation d'alcoyl-9 dioxo-1,8 décahydroacridines fluorescentes en bleu en milieu acide, en jaune-vert en milieu alcalin.

Réactif. On dissout 0,25 g de cyclohexane dione-1,3, 10 g d'acétate d'ammonium et 5 ml d'acide acétique dans 80 ml d'eau et complète à 100 ml par l'eau.

Mode opératoire. A 3 ml de solution aqueuse d'aldéhyde, on ajoute 1 ml de réactif, chauffe pendant 1 h à 60°, refroidit pendant 2 mn dans un bain d'eau-glace et ajoute, soit 1 ml d'eau (fluorescence bleue), soit 1 ml de lessive de soude 36° Bé (fluorescence jaune-vert).

Lecture à l'excitation 366 mμ, émission 470 mμ en milieu acide, excitation 436 mμ et émission 520 mμ en milieu alcalin.

Etalons: pour la fluorescence bleue, solution de dioxo-1,8 décahydroacridine dans l'eau à 2% d'éthanol; pour la fluorescence jaune-vert, solution de dioxo-1,8 décahydroacridine dans le mélange: éthanol 2 ml, lessive de soude 20 ml, eau q.s.p. 100 ml.

Applications

Voir Tableau VII.

TABLEAU VII

	Limites du dosage, µg	Lecture 50 Essai, µg	Lecture 50 Etalon, µg/ml
Lecture en milieu acide			
Formaldéhyde	0,5–2,5	1,0	0,51
Acétaldéhyde	0,2–1,0	0,45	0,56
Propionaldéhyde	0,3–1,5	0,62	0,44
Butyraldéhyde	0,6–3,0	1,20	0,47
Lecture en milieu alcalin			
Formaldéhyde	0,5–2,5	1,05	0,64
Acétaldéhyde	0,2–1,0	0,45	0,80
Propionaldéhyde	0,2–1,0	0,38	0,51
Butyraldéhyde	0,5–2,5	1,0	0,60

Remarque. L'isobutyraldéhyde, le citral, le glyoxal et l'acide glyoxylique réagissent beaucoup plus faiblement. Le benzaldéhyde peut être dosé entre 2 et 10 µg, avec émission à 455 mµ en milieu acide, lecture 50 pour 4 µg.

Aldéhydes en R—CH_2—CHO

Principe. Formation d'une dialcoyl-2,3 carboxy-5 amino-7 quinoléine, par action de l'acide diamino-3,5 benzoïque en milieu phosphorique; fluorescence jaune-vert.

Réactif. A 2 g de dichlorhydrate d'acide diamino-3,5 benzoïque, on ajoute 10 ml d'acide phosphorique (d = 1,62) et dilue à 20 ml par l'eau.

Mode opératoire. A 2 ml de solution aqueuse d'aldéhyde, on ajoute 2 ml de réactif. On chauffe pendant 30 mn à 50° à l'abri de la lumière vive, laisse refroidir à température ordinaire et ajoute 2 ml d'eau. Lecture à l'excitation 405 mµ, émission 495 mµ.

Etalon: solution de méthyl-2 carboxy-5 amino-7 quinoléine dans l'acide acétique dilué à 10% v/v par l'eau.

Applications

Voir Tableau VIII.

TABLEAU VIII

	Limites du dosage, µg	Lecture 50 Essai, µg	Lecture 50 Etalon, µg/ml
Acétaldéhyde	2–10	5,7	0,31
Propionaldéhyde	2–10	5,7	0,23
Butyraldéhyde	2–10	5,7	0,19

2-*Désoxy oses*

Principe. Voir: Aldéhydes en R—CH_2—CHO

Réactif. A 2 g de dichlorhydrate de l'acide diamino-3,5 benzoïque en solution dans 57 ml d'eau, on ajoute 43 ml d'acide phosphorique (d = 1,71).

Mode opératoire. A 2 ml de solution aqueuse d'un désoxy-2 ose, on ajoute 2 ml de réactif, bouche les tubes par un tampon de coton et chauffe pendant 15 mn au bain-marie bouillant, à l'abri de la lumière vive. Lecture après 2 mn de repos dans un bain d'eau-glace, à l'excitation 405 mµ, émission 505 mµ.

Etalon: solution de méthyl-2 carboxy-5 amino-7 quinoléine dans l'acide acétique dilué à 10% v/v par l'eau.

Applications

Voir Tableau IX.

TABLEAU IX

	Limites du dosage, μg	Lecture 50 Essai, μg	Etalon, $\mu g/ml$
2-Désoxy ribose	10–50	21	0,025
Digitoxose	20–100	44	0,030,

Acides α,β-dihydroxylés

Principe. Par oxydation periodique, formation d'acide glyoxylique révélé par condensation sur le résorcinol. La lactone formée s'oxyde à l'air en milieu alcalin: fluorescence jaune-vert.

Réactifs. (*a*) Solution aqueuse 0,05*M* de métaperiodate de sodium, ajustée à pH 10 par la soude *N*. (*b*) Solution 0,1*N* d'arsénite de potassium (anhydride arsénieux, 4,945 g; solution *N* de potasse, 75 ml; bicarbonate de potassium, 40 g; eau, q.s.p. 1000 ml). (*c*) A 50 ml de solution 0,1*N* de nitrate d'argent, on ajoute 5 ml de soude *N*. On lave le précipité par décantation, puis dissout et complète à 150 ml avec de la solution *N* d'acide sulfurique. (*d*) Solution aqueuse à 2% de résorcinol. (*e*) Solution aqueuse saturée de bicarbonate de potassium.

Mode opératoire. A 1 ml de solution aqueuse neutralisée d'acide α,β-dihydroxylé, on ajoute 0,2 ml de réactif *a* et, après 15 mn de repos à température ordinaire, 0,5 ml de réactif *b*. Après 20 mn de repos à température ordinaire, on ajoute 0,3 ml de réactif *c*, agite, dilue par 1 ml d'eau et filtre. A 1 ml du filtrat, on ajoute 1 ml d'acide chlorhydrique concentré (d = 1,19) puis 0,5 ml de réactif *d*. On chauffe pendant 20 mn à 60°, laisse refroidir dans un bain d'eau à température ordinaire, ajoute lentement en agitant 5 ml de réactif *e* et chauffe à 60° pendant 15 mn. On laisse refroidir à température ordinaire. Lecture à l'excitation 436 mμ émission 530 mμ.

Etalon: solution aqueuse de fluorescéine sodique.

Applications

Voir Tableau X.

TABLEAU X

	Limites du dosage, μg	Lecture 50 Essai, μg	Etalon, $\mu g/ml$
Acide tartrique	1–5	2,1	0,13
Acide mucique	1–5	2,3	0,076
Acide galacturonique (1 H_2O)	2–10	4,7	0,077
Acide glucuronique	2–10	4,5	0,068

Phénols

Principe. Condensation sur l'acétylacétate d'éthyle en milieu sulfurique, avec formation de coumarine: fluorescence bleue à bleu-vert.

Réactif. Solution à 2% v/v d'acétylacétate d'éthyle dans l'éthanol.

Mode opératoire. A la prise d'essai en solution dans 1,5 ml d'alcool, on ajoute 1 ml de réactif puis 2,5 ml d'acide sulfurique concentré, très lentement, en faisant couler l'acide le long de la paroi du tube et en agitant. Lecture après 15 mn de repos à température ordinaire, à l'excitation 366 mμ.

Etalon: solution de sulfate de quinine dans l'acide sulfurique 0,1*N*.

Applications

Voir Tableau XI.

TABLEAU XI

	λ d'émission, $m\mu$	Limites du dosage, μg	Lecture 50 Essai, μg	Etalon, $\mu g/ml$
Phénol*	460	100–400	120	0,18
Pyrocatéchol	495	10–45	15	0,16
Gaïacol	495	10–50	20	0,24
Résorcinol	430	0,07–0,38	0,17	0,34
Phloroglucinol	490	2–8	3,5	0,33
Hydroquinone†	475	6,2–19	6,2 → 60	0,14 → 60

* Après addition de l'acide sulfurique, on porte pendant 15 mn à 80° puis refroidit pendant 3 mn dans un bain d'eau-glace avant lecture.

† La droite n'est obtenue qu'au-delà de la lecture 60.

Summary—By means of suitable chemical reactions, formaldehyde is obtained from 1,2-diols, hexitols, primary α-amino alcohols, 2-nitro-1-hydroxy aliphatic compounds, the methylene group in R—CH=CH_2 and 17-ketolsteroids, and converted into a dihydrolutidine derivative which is then determined by fluorimetry. The formation of dihydropyridine derivatives also allows the fluorimetric determination of primary alkylamines, nitriles and aliphatic aldehydes. Aldehydes with an α-methylene group and 2-deoxysugars can be determined by forming fluorescent quinaldines. The fluorescent compound obtained by condensing glyoxylic acid with resorcinol allows the determination of α,β-dihydroxy and hexuronic acids after a periodate oxidation. The fluorimetric determination of phenols is achieved by converting them into coumarins.

Zusammenfassung—Durch geeignete chemische Reaktionen erhält man Formaldehyd aus 1,2-Diolen, Hexiten, primären α-Aminoalkoholen, 2-Nitro-1-hydroxy-aliphaten, der Methylengruppe in R—CH=CH_2 und 17-Ketolsteroiden; der Formaldehyd wird in ein Dihydrolutidinderivat überführt, das dann fluorimetrisch bestimmt wird. Die Bildung von Dihydropyridinderivaten erlaubt auch die fluorimetrische Bestimmung von primären Alkylaminen, Nitrilen und aliphatischen Aldehyden. Aldehyde mit α-Methylengruppe und 2-Desoxyzucker können durch Bildung fluoreszierender Chinaldine bestimmt werden. Das fluoreszierende Produkt der Kondensation von Glyoxylsäure mit Resorcin erlaubt die Bestimmung von α,β-Dihydroxy- und Hexuronsäuren nach Perjodatoxidation. Phenole werden fluorimetrisch bestimmt durch Umwandlung in Cumarine.

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NEUTRON ACTIVATION ANALYSIS BY STANDARD ADDITION AND SOLVENT EXTRACTION

DETERMINATION OF IMPURITIES IN ALUMINIUM

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Summary—A separation scheme based on selective extraction in conjunction with the standard addition technique has been developed for the determination of impurities in aluminium by neutron activation. Preliminary investigations have been carried out on the extractability of Sc, Co, Hf, Fe, Sn, Cd, Zn, Ag, Cr, Ce, Cs and Rb by TDA and TBP from acidic media. The best conditions are predicted for the separation of these elements into fractions suitable for analysis by gamma-ray spectrometry. Recovery values of ~90% were obtained for all the elements.

IN activation analysis, special techniques other than those involving the addition of inactive carriers have been used for yield determination. One such technique is the addition of a known amount of a carrier-free radioactive tracer to the sample after the irradiation.[1] When chemical yield corrections cannot be made owing to a lack of suitable carriers or tracers, the yields from standards and samples must be quantitative or equal. Selective and quantitative procedures have been proposed for the analysis of many elements.[2–4] In order to ensure equal yields from standards and samples a new method was developed previously.[5] The principle of the new approach and data on its application to the determination of uranium in aluminium and rocks were also reported.[6] In the present paper a general scheme has been developed for the radiochemical separation and analysis of the induced radionuclides in aluminium.

Many separation schemes, based on sequential ion-exchange fractionation, have been proposed for the activation analysis of impurities in aluminium.[2,7–9] The procedures involved however, are lengthy, even when automated. In the present study work has been carried out on elements giving rise to long-lived radioactive isotopes. Details of the elements are presented in Table I.

TABLE I

Element	Radioisotope determined	Half-life	Gamma energy, *MeV*
Scandium	^{46}Sc	85 d	0·89, 1·12
Cobalt	^{60}Co	5·3 y	1·17, 1·33
Hafnium	^{181}Hf	46 d	0·13, 0·34, 0·48
Iron	^{59}Fe	45·1 d	1·10, 1·29
Tin	^{113}Sn	112 d	0·39
Zinc	^{65}Zn	245 d	0·51, 1·12
Mercury	^{203}Hg	47 d	0·279
Silver	^{110}Ag	270 d	0·45, 0·68, 0·88, 1·39, 1·52
Chromium	^{51}Cr	27·8 d	0·32
Caesium	^{134}Cs	2·3 y	0·60, 0·79
Rubidium	^{86}Rb	18·6 d	1·08

Other elements that also give long-lived radionuclides are not included in the scheme because they are present at concentrations beyond determination. The extractability of some has, however, been studied.

EXPERIMENTAL

Irradiation

Aluminium samples (taken from the cans used for pile irradiation) were washed with dilute nitric acid, water and acetone and then dried. The chemicals used as standards were of high analytical purity including scandium oxide, cobalt nitrate, iron oxide, cadmium oxide, tin and zinc metals, silver nitrate, mercuric oxide, cerium oxide, chromic oxide, caesium and rubidium chlorides. Aluminium samples were carefully enclosed in thin aluminium foil. Suitable amounts of the standards in the solid form were weighed on ashless filter paper discs (about 2 cm diameter); the discs were carefully folded and enclosed in thin aluminium foil. Samples and standards were subsequently placed together in an aluminium can and irradiated in the UA-RR-1, 2MW Research Reactor at Inshas for 48 hr. The thermal flux is approximately $1{\cdot}3 \times 10^{13}$ neutrons/cm^2/sec. Samples were left to cool for about 10 days after irradiation to allow for decay of the induced short-lived activities.

Reagents

Tributylphosphate (TBP) was purified by washing with 5% sodium carbonate solution and water. Tri-n-dodecylamine (TDA), a high-purity product of Rhône-Poulenc, France, was used without further purification. TBP and TDA were used in the form of 50% and 20% solutions respectively, in xylene.

Apparatus

An ECKO scintillation counter with a $1{\cdot}75 \times 2$ in. sodium iodide (thallium) crystal (well-type) was used for determining the gross activity of the organic and aqueous phases and studying the extractability of the different components under various conditions.

A nuclear Chicago Single-Channel Model 132B analyser, with a 3×3 in. sodium iodide (thallium) crystal was used for measuring the photo-peak activities and the gamma-spectra.

Extraction experiments

The extractability of the various metals in the different extraction systems was studied by mixing the aqueous solutions of the given tracers with equal volumes (usually 5 ml) of the organic solvents till equilibrium was reached (about 30 min). Separation of the phases was enhanced by contrifugation. The degree of extraction was calculated by measuring the radioactivity of the tracer in both phases.

Extraction separations were carried out in pear-shaped separating funnels by shaking a known volume (usually 10 ml) of the sample solution or the subsequently separated fraction with the solvent or the stripping solution until equilibrium was attained ($\sim$1 min).

Processing of samples and standards

Solutions of irradiated aluminium samples (50 ml) were prepared by dissolving known amounts in concentrated hydrochloric acid to which had been added a few drops of concentrated nitric acid, heating to near dryness and then making about $1{\cdot}5M$ in hydrochloric acid and about $2{\cdot}5M$ in aluminium chloride. If a residue appeared the solution was filtered, and the residue was washed with a little acid until it was free from activity. Standards in the filter paper discs were carefully removed from the aluminium foil, transferred to 100-ml beakers and dissolved (see Table II). Each standard solution was filtered through a small sintered-glass filter, and the residue (filter paper disc) was washed several times with the solvent till free from activity. The filtrate and washings were then transferred back to the beaker, evaporated to near dryness, treated with about 10 ml of hydrochloric acid (1 + 1) (1N nitric acid in the case of Ag and Hg) and finally transferred to 50-ml graduated flasks. The beaker was washed several times (till free from activity) with the appropriate acid and the washings were transferred to the flask; the solution was then made up to the mark with the appropriate acid.

Procedures for dissolving the irradiated elements or compounds used in the preparation of standard solutions and tracers are presented in Table II.

Mechanism and conditions of extraction

In the method proposed by Růžička, Starý *et al.*,[10,11] designated substoichiometry, the induced radionuclide is selectively isolated from the sample solution and the standard by using a controlled amount of reagent in quantity less than that stoichiometrically corresponding to the amount of the

TABLE II.—PROCEDURES FOR PREPARING STANDARDS

Irradiated material	Amount,* *mg*	Procedure
Sc_2O_3	1	Boil with 5 ml HCl(1 + 1), add H_2O_2, dilute with HCl(1 + 1)
$Co(NO_3)_2$†	5	HCl(1 + 1)
Fe_2O_3	50	HCl(1 + 1)
Sn	‡	conc. HCl, dilute with HCl(1 + 1)
CdO	8	HCl(1 + 1)
Zn	50	HCl(1 + 1)
HgO	‡	1*N* HNO_3
$AgNO_3$†	5	1*N* HNO_3
CeO_2	2	conc. HNO_3, H_2O_2, dilute with HCl(1 + 1)
Cr_2O_3	8	HCl(1 + 1)
CsCl‡	1	HCl(1 + 1)
RbCl†	1	HCl(1 + 1)

* As metal.

† Weighed quantities of these compounds dissolved in dilute acid are standardized by suitable analytical methods.

‡ The amounts taken are not known.

element to be separated. Extraction with TDA and TBP is governed by a mechanism different from that governing extraction with chelating agents, since in the latter case extraction is mainly dependent on the hydrogen ion concentration and there is a threshold pH-value at which the best extraction is obtained.[12] Extraction with TDA and TBP, on the other hand, varies with change in the concentrations of acid, salting-out agents, and different anions and cations.[13–19] The application of such solvents therefore necessitates the extraction of the element under study from the sample solution and from the standard under the same conditions, and this can be achieved by the standard addition technique. Preliminary studies have shown that keeping a constant aqueous phase composition ensures that the same amount of the metal is always separated into the organic phase, with high precision. Data in Table III verify this for scandium extraction. Analogous results were obtained for the other radioisotopes.

TABLE III.—EXTRACTION OF ^{46}Sc

Original Sc activity, *cpm/ml*	Activity extracted, *cpm/ml*	Extraction, %
3244 ± 46	2704 ± 41	83·8
6080 ± 91	5055 ± 70	83·0
1698 ± 22	1411 ± 21	83·0
860 ± 14	712 ± 12	82·5

Moreover both accuracy and reproducibility are maintained for micro as well as macro concentrations. Because activation analysis deals basically with the determination of minute quantities of elements the change in the element concentration at such levels does not affect the degree of extraction. The extractability of a given element must also not be affected by the addition of minute amounts (of the order of the concentration of the standard) of other extractable elements. The solvent concentration is therefore selected so that at equilibrium the free solvent molarity is the same for extraction from a sample solution and that to which the standards have been added. This condition can be fulfilled by using higher solvent molarities. Preliminary studies have shown that the use of 20% TDA and 50% TBP satisfies this requirement. In Table IV are presented data on the extractability of the isotopes studied from a chloride medium with 20% TDA before and after spiking the solution (10 ml) with 1 ml of hydrochloric acid (1 + 1) containing 1, 5, 50, 8, 50, 1, 5, 2, 8, 1 and 1 μg/ml of Sc, Co, Fe, Sn, Cd, Zn, Hg, Ag, Ce, Cr, Cs and Rb, respectively.

TABLE IV.—EFFECT OF ADDITIVES ON EXTRACTABILITY; AQUEOUS PHASE: ~1·5*M* HCl; ~2·5*M* $AlCl_3$

Radioisotope	Extraction, %	
	before addition*	after addition
Cr	2·0	1·8
Hf	97·5	98·0
Co	96·0	94·5
Fe	99·0	98·0
Sn	98·0	98·0
Cd	85·0	81·0
Zn	99·5	99·5
Hg	99·0	99·0
Ag	92·0	93·0
Ce	2·0	2·0
Cs	0·5	0·5

* The aqueous phase was spiked with 1 ml of HCl(1 + 1) containing no additives.

Extractability and separation

Extraction of metals from various acidic media by TDA and TBP has already been investigated.[12,20] In the present paper data were obtained on the extractability of the given metals by TDA and TBP from different aqueous media in order to choose the best conditions of separation. The results presented in Tables V and VI show the degree of extraction from the aqueous solutions finally selected for the separation scheme.

From these results it is clear that with the exception of scandium, cerium (which was taken as representative of the other rare earths) chromium and the alkali metals, the elements are extracted almost quantitatively with TDA from 2·5*M* aluminium chloride–1·5*M* hydrochloric acid. Among

TABLE V.—EXTRACTION BY 20% TDA

Element	Extraction, %, from			
	2·5*M* $AlCl_3$ + 1·5*M* HCl	2*M* HCl	3*M* HF + 0·5*M* HCl	1*M* HNO_3
Scandium	1	—	—	—
Hafnium	98	1	—	—
Cobalt(II)	97·5	1	—	—
Iron(III)	99	96	3	—
Tin(IV)	98	99	8	—
Cadmium	89	98	25	50
Zinc	97	99	97	3·5
Mercury(II)	99	99	98	99
Silver	92	95	94	96·6
Cerium(III)	1·5	—	—	—
Chromium	1·3	—	—	—
Caesium	1	—	—	—
Rubidium	1	—	—	—

TABLE VI.—EXTRACTION BY 50% TBP FROM 2·5*M* $AlCl_3$ + 1·5*M* HCl

Element	Extraction, %
Scandium	82
Cerium(III)	1
Chromium	2
Caesium	1
Rubidium	1

the elements that are extracted from this medium only hafnium and cobalt are not extracted by TDA from 2*M* hydrochloric acid; among the rest only iron and tin are not extracted from 3*M* hydrofluoric acid–0·5*M* hydrochloric acid and finally zinc is not extracted from 1*M* nitric acid.

Mercury and silver are almost quantitatively extracted from all media. Cadmium is partially extracted with TDA from 3*M* hydrofluoric acid–0·5*M* hydrochloric acid and from 1*M* nitric acid. From the elements that are not extracted with TDA from aluminium chloride–hydrochloric acid medium only scandium is extracted with TBP and can be selectively isolated with the latter.

Preliminary studies were also performed on the extraction of the induced isotopes from 10 ml of the irradiated aluminium sample solution in 2·5*M* aluminium chloride–1·5*M* hydrochloric acid. About 50% of the total gross activity is extracted by two 5 ml portions of TDA, 44% is subsequently extracted by two 5 ml portions of TBP and only ~6% of the total activity remains finally in the aqueous phase. This residual activity is from the isotopes induced from chromium, the rare earths and the alkali metals.

Procedure

The steps of the separation scheme are outlined in Fig. 1 and are described in more detail below.

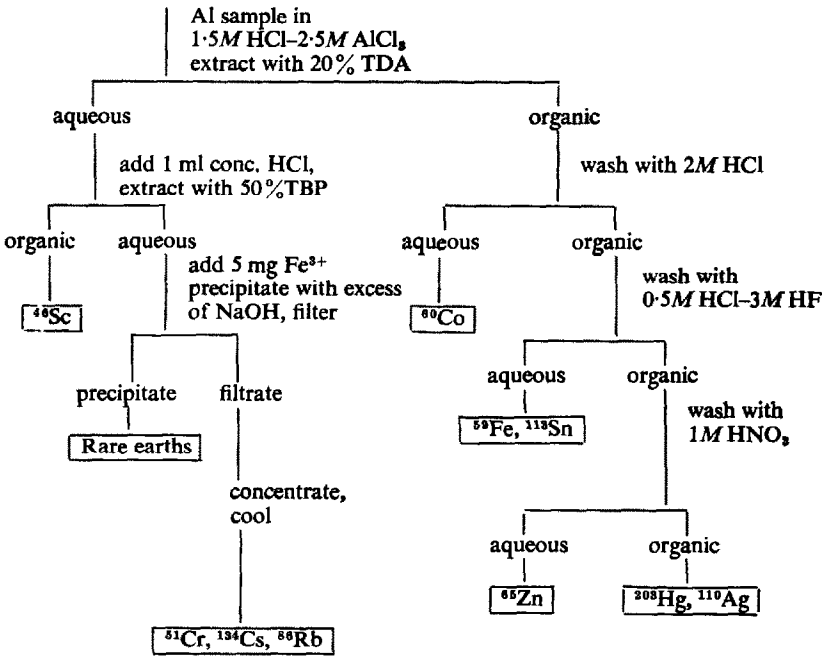

FIG. 1.—Separation scheme.

Take two equal aliquots (usually 10 ml) of the sample solution in two separating funnels (labelled 1 and 1′); add carefully to the first (solution A) 500 μl of hydrochloric acid (1 + 1) and 100 μl of 1*N* nitric acid and to the second (solution B) 50 μl of each standard solution. The acid content of the two solutions is thus equal. The amount of the standard may be varied according to the expected content in the sample. Transfer 5 ml of 20% TDA solution to each of the funnels, stopper then, shake them vigorously for 1 min and allow to stand until separation of the phases is complete (usually 3–5 min). Withdraw the aqueous phases into two other separating funnels (labelled 2 and 2′). Repeat the extraction with 5 ml of 20% TDA, allow to stand and separate the phases. Transfer the aqueous phases to two other separating funnels (labelled 3 and 3′), and add the organic phases to the first extracts in funnels 1 and 1′. According to the data in Table V the collected extracts contain almost all the induced Hf, Co, Fe, Sn, Cd, Zn, Hg and Ag activities.

Add 1 ml of concentrated hydrochloric acid and 5 ml of 50% TBP to each aqueous phase in funnels 3 and 3′, shake vigorously for about 1 min and allow the phases to separate; transfer the aqueous phases to funnels 2 and 2′ and the organic phases to two counting vials. Add 1 ml of concentrated hydrochloric acid to each aqueous phase, repeat the extraction with 5 ml of 50% TBP

and separate the phases. Transfer the aqueous phases to funnels 3 and 3′ for a third extraction with TBP in the case of higher scandium content or otherwise to two 100 ml beakers. Add the organic phases to the first TBP extracts in the counting vials (scandium).

Add 10 ml of 2*M* hydrochloric acid to the combined extracts from the first extraction in funnels 1 and 1′, shake for 1 min and allow the phases to separate. Withdraw the aqueous phases into two counting vials. According to the data in Table V the collected aqueous solutions should contain ~99% of the hafnium and cobalt present in the sample together with negligible proportions of iron and silver.

Add 10 ml of 3*M* hydrofluoric acid–0·5*M* hydrochloric acid to each of the organic phases from the previous extraction. Shake the funnels for 1 min, allow the phases to separate and withdraw the aqueous phases into counting vials (iron and tin). About 72% of cadmium, if present, will be recovered in this fraction.

Add 10 ml of 1*N* nitric acid to the organic phases in the funnel from the previous extraction, shake for 1 min, separate the phases and withdraw the aqueous solutions into counting vials (zinc).

Collect the organic phases from the previous extraction into two counting vials (silver and mercury).

Chromium, rare earths and the alkali metals are present in the aqueous phase from the second extraction. Check that no significant amount of scandium is left. This fraction may be analysed as recommended by Girardi and Pietra.[2]

Quantitative analysis

The quantitative determination of the elements by this method has been carried out by measuring the respective photo-peak activities in the fractions obtained. For this purpose identical vials were used and counting was done under the same geometrical conditions. The amount of metal (x) to be determined is calculated from:

$$x = \frac{x_s A}{(A_m - A)} \tag{1}$$

where x_s = the amount of metal in the added standard solution, A and A_m are the photo-peak activities in two fractions isolated from the sample (solution A) and from the sample to which is added the irradiated standard (solution B), respectively.

The validity of the method has been assessed by varying the value of x_s, *i.e.*, the amount of standard added, and then calculating the value of x. A calculated amount of acid was always added to solution A so as to make its composition the same as solution B. In the case of the presence of significant weighable) amounts of the elements to be determined and consequently the necessity of adding comparable amounts of standards, it is recommended to spike solution A with the calculated quantities of acid containing the same concentrations of unirradiated standards; this ensures equal yields from solutions A and B.

RESULTS AND DISCUSSION

The gamma-spectrum of an irradiated aluminium sample (Fig. 2) exhibited prominent peaks at 0·88 and 1·1 MeV. The gamma spectra of the isolated fractions show the photopeaks of the respective radionuclides. The spectra presented correspond to fractions isolated about two months after irradiation. It was found, however, that analysis can be performed 10–15 days after irradiation without any significant differences in the results, and better sensitivity is obtained. Curves 1 and 2 in Figs. 3–8 represent the gamma-spectra of the fractions obtained from two equal sample aliquots (12 ml containing 0·94 g of Al), one of which was spiked with 50, 150, 1500, 250, 150, 50, 200 and 100 μl of Sc, Co, Fe, (Sn), Zn, Ag, (Hg) and Cr irradiated standard solutions respectively, (curves 2); the equivalent amount of acid (2250 μl of hydrochloric acid (1 + 1) and 250 μl of 1*M* nitric acid) was added to the other solution (curves 1). separation was then completed as described. Tin-113 and mercury-203 isotopes were added in order to verify their separation by the given scheme. Results obtained on the quantitative analysis of trace elements in aluminium by standard addition and solvent extraction are presented in Table VII.

The rubidium concentration was evaluated from the relative activities of ^{51}Cr and ^{86}Rb as follows. The saturation activity of ^{51}Cr and ^{86}Rb (in disintegrations/min) obtained by the irradiation of 1 μg of the element in a flux of 10^{12} n cm^{-2} sec^{-1} is

TABLE VII.—QUANTITATIVE DETERMINATION OF IMPURITIES IN ALUMINIUM BY NEUTRON ACTIVATION

Element	Concentration, *ppm*	
	Standard addition*	Conventional method†
Sc	1·07	1·19
Co	7·70	8·15
Hf	beyond detection	beyond detection
Fe	1450	1280
Zn	126	109
Ag	3·2	2·9
Cr	2·5	3·0
Cs	beyond detection	beyond detection
Rb	0·5†	not determined
Rare earths	beyond detection	beyond detection

* Average of 2–5 determinations.
† Average of 2 determinations.
‡ Calculated from nuclear data.

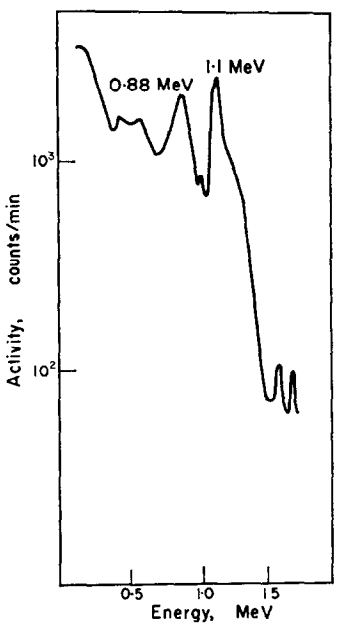

FIG. 2.—Gamma-ray spectrum of irradiated aluminium sample.

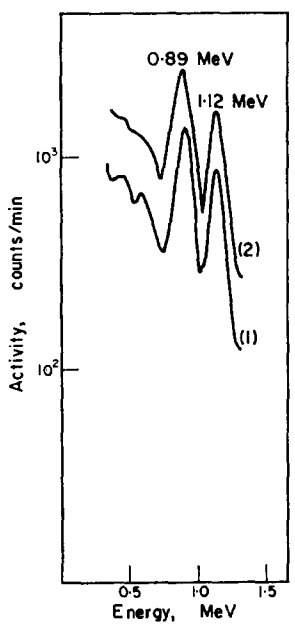

FIG. 3.—Gamma-ray spectrum of the TBP extract (^{46}Sc).
(1) Sample, (2) Sample + standards.

$4{\cdot}1 \times 10^5$ and $2{\cdot}4 \times 10^5$, respectively. The corresponding activity for the photo-peaks at 0·325 and 1·08 MeV is $1{\cdot}4 \times 10^4$ and $2{\cdot}6 \times 10^3$ respectively.[2] The ratio of the two photo-peak activities is then equal to 5·4. This ratio is not changed by changing the neutron flux. For 48-hr irradiation, where the growth factors (A_t/A_∞) for ^{51}Cr and ^{86}Rb are 0·05 and 0·07, respectively, this ratio will be 3·86. After two months' decay the ratio becomes approximately 8. The ratio of the photo-peak activities of the isolated ^{51}Cr and ^{86}Rb is seen from Fig. 8 to be about 90; then the Rb concentration can be evaluated as about 0·5 ppm.

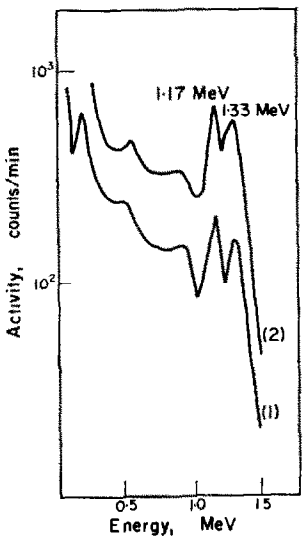

FIG. 4.—Gamma-ray spectrum of the 2*M* HCl stripping solution (^{60}Co).
(1) Sample, (2) Sample + standards.

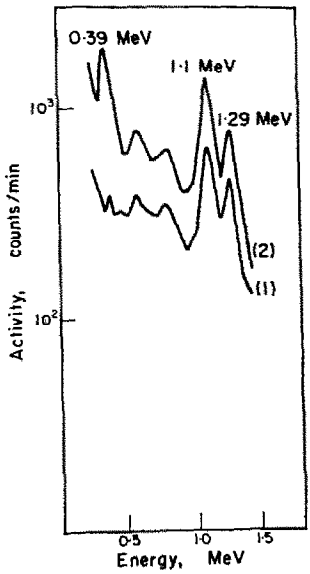

FIG. 5.—Gamma-ray spectrum of the 3*M* HF–0·5*M* HCl stripping solution (^{59}Fe, ^{113}Sn)
(1) Sample, (2) Sample + standards.

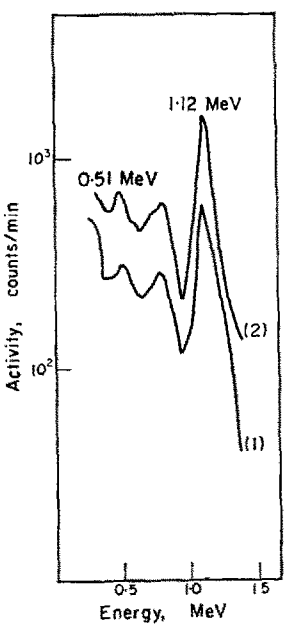

FIG. 6.—Gamma-ray spectrum of the 1*N* HNO_3 stripping solution (^{65}Zn).
(1) Sample, (2) Sample + standards.

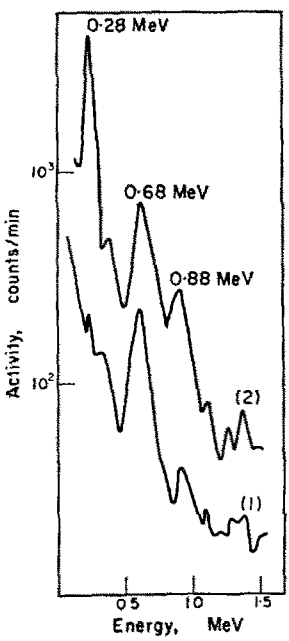

FIG. 7.—Gamma-ray spectrum of the scrubbed TDA extract (^{110}Ag, ^{203}Hg).
(1) Sample, (2) Sample + standards.

The tin and mercury concentrations may be similarly calculated on the basis of the iron and silver concentrations determined, but only after correcting for the activity resulting from the higher-energy components ^{59}Fe and ^{110}Ag (Figs. 5 and 7).

Although a check on the half-lives has been made by measuring the photo-peak activities for some of the nuclides (^{86}Rb, ^{51}Cr, ^{59}Fe) at varying intervals of time within 2–5 months, the identities of the product nuclides have been confirmed by comparing the shapes of the photo-peaks with those of irradiated reference standards.

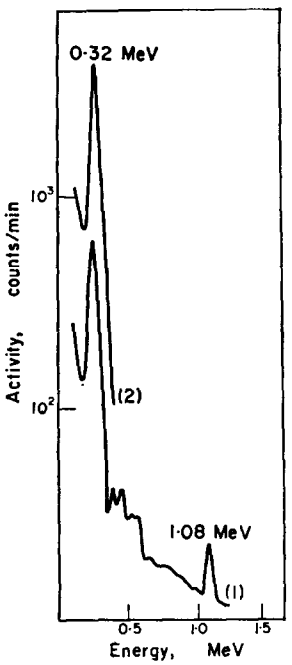

FIG. 8.—Gamma-ray spectrum of the aqueous phase (^{51}Cr, ^{86}Rb).
(1) Sample, (2) Sample + standards.

As expected from the data in Tables V and VI difficulties due to cross-contamination are not serious in the given concentration range. Although interference from other long-lived nuclides, not included in the scheme, has not been considered, they are expected (from available extraction data) to contaminate only some of the fractions and to be subsequently separable. Thus the gamma spectrum presented in Fig. 4 shows beside the photo-peaks of ^{60}Co another low-energy component (at 0·31 MeV), which is most probably ^{233}Pa produced from thorium. It follows from the other gamma spectra that aluminium does not contain other interfering elements. In the application of the scheme for the determination of these elements in more complex materials such as rocks and soils, further studies will be required in order to take care of other interferences. Additional extraction or elution steps will be also required in the case of higher content of one of the elements in order to minimize contamination of the subsequent fractions.

The results obtained by the method standard addition and solvent extraction agree well with those obtained by the conventional method.

The results obtained on the determination of scandium and zinc in aluminium by the

standard addition technique are presented in Tables VIII and IX. These results show that the method gives satsifactory precision.

The method reported can also be used for the rapid determination of individual elements and in that respect it is also more simple and selective than the other methods. Thus for the determination of scandium, for example, samples are irradiated together with a scandium standard and the chemical procedure consists of: (1) processing of samples and the standard as described before, (2) preliminary separation of hafnium, cobalt, iron, tin, zinc, cadmium, silver and mercury by extraction with TDA and (3) selective extraction of scandium with TBP.

From the relative activities isolated (see the photo-peaks in Figs. 3–8) it is to be noted that most of the induced activity in aluminium is due to the presence of scandium, zinc, chromium, iron, cobalt and silver. Moreover the activity produced decreases in the order given. Fortunately the elements mentioned are isolated by the method given with a very high selectivity and they could be determined with a high precision (see Tables VIII and IX). The remaining elements are determined with lower

TABLE VIII.—DETERMINATION OF SCANDIUM BY THE STANDARD ADDITION TECHNIQUE

Weight of sample, *g*	Standard Sc added, *μg*	*A*,* *cpm*	A_m,† *cpm*	Sc found, *μg*
0·783	0·2	7290	9092	1·02
0·783	0·5	7302	10933	1·28
0·783	0·7	7215	13954	0·96
0·783	1·0	6738	14233	1·15
0·940	1·0	7751	16376	0·95
			mean	0·95

* Activity of the 0·89-MeV photo-peak of ^{46}Sc extracted from sample.

† Activity of the 0·89-MeV photo-peak of ^{46}Sc extracted from sample and standard.

TABLE IX.—DETERMINATION OF ZINC BY THE STANDARD ADDITION TECHNIQUE

Weight of sample, *g*	Standard Zn added, *μg*	*A*,* *cpm*	*A*,† *cpm*	Zn found, *μg*
0·783	25	2625	3215	142
0·783	50	2644	3935	131
0·783	100	2612	5558	114
0·783	150	2589	6985	115
0·940	150	3008	6762	127
			mean	126

* Activity of the 1·12-MeV photo-peak of ^{65}Zn isolated from sample.

† Activity of the 1·12-MeV photo-peak of ^{65}Zn from sample and standard.

precision; these elements are of less importance, however, since they make only a small contribution to the induced activity in aluminium. The sensitivity of this method is very high for most of the elements given and can be further increased by carrying out the analysis immediately after the decay of the short-lived activities.

Zusammenfassung—Ein Trennungsgang zur Bestimmung der Verunreinigungen in Aluminium durch Neutronenaktivierung wurde entwickelt. Er beruht auf selektiver Extraktion und dem Zustatz eines Standards. Es wurden Voruntersuchungen über die Extrahierbarkeit von Sc, Co, Hf, Fe, Sn, Cd, Zn, Ag, Cr, Ce, Cs und Rb mit TDA und TBP aus sauren Medien ausgeführt. Die optimalen Bedingungen zur Trennung dieser Elemente in zur Analyse durch Gamma-Spektrometrie geeignete Fraktionen werden vorhergesagt. Für alle Elemente wurden Ausbauten über 90% erzielt.

Résumé—On a élaboré un schéma de séparation basé sur l'extraction sélective en liaison avec la technique d'addition d'étalon pour le dosage des impuretés dans l'aluminium par activation de neutrons. Des essais préliminaires ont été menés sur l'extractibilité de Sc, Co, Hf, Fe, Sn, Cd, Zn, Ag, Cr, Ce, Cs et Rb par le TDA et le TEP à partir de milieux acides. On laisse prévoir les meilleures conditions pour la séparation de ces éléments en fractions convenant à l'analyse par spectrométrie de rayons gamma. On a obtenu des valeurs de récupération ~90% pour tous les éléments.

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SHORT COMMUNICATIONS

Photometrische Bestimmung von Kupfer mit Polyäthylenimin

(*Eingegangen* 6 *März* 1967. *Angenommen* 18 *April* 1967)

PHOTOMETRISCHE Bestimmungen von Kupfer(II)-Koordinationsverbindungen erfordern unbequeme Abtrennungen von den Ionen Al(III), Fe(III), Cr(III), sowie auch von Ni(II), Co(II), Mn(II), sofern mit Ammoniak oder auch Aminen, wie Tetraäthylenpentamin,[1] gearbeitet wird.

Polyäthylenimine (PEI) bilden nach Thiele und Gronau[2] mit Cu(II) Komplexe, in denen der Stickstoff des PEI als Donator fungiert. Die Untersuchung der Reaktion von PEI mit anderen Übergangsmetallionen zeigte nunmehr, dass eingangs genannte Ionen und auch Mg(II), Hg(II), Pd(II) *etc.* insbesondere bei Reagensüberschuss auch bei pH 7 keine schwerlöslichen Produkte liefern.

PEI zeigt allgemein die Reaktionen sekundärer Amine. Es liefert mit Schwefelkohlenstoff in Wasser schwerer lösliche Carbate,* die mit Natriumcarbonat oder verd. Alkalilaugen aber leicht in Lösung gebracht werden können. Salpetrige Säure reagiert mit PEI unter Nitrosamin-Bildung und Abscheidung gelblicher Produkte.* Quecksilberjodid und Arsen(III)sulfid werden ebenso gelöst, wie dies auch durch andere sekundäre Amine, z.B. Dibutylamin, erfolgt.

Die Farbreaktion mit Cu(II) (λ_{max} 645 mμ) zeigt Konstanz im pH-Bereich 2,5–7,0. Die Gegenwart von 2% Natriumchlorid in Probelösungen erhöht den Extinktionskoeffizienten ($\varepsilon = 230$) im pH-Gebiet 3–5, und dieser zeigt dann in Lösungen bis zu 10%ig an Natriumchlorid keine Veränderung mehr. Der Erhöhung des Extinktions-koeffizienten ist auf den Abbau der Wasser-Koordination zurückzuführen. Abhängigkeiten der Lage λ_{max} vom Reagensüberschuss, wie diese für die Reaktionen von Cu(II) mit Ammoniak bzw. Äthylendiamin zu beobachten sind, treten bei der Benutzung von PEI nicht auf. Der Extinktions-koeffizient übertrifft die der Kupfer-Ammin-Reaktion um das Fünffache. Die Farb-Konstanz beträgt innerhalb der Grenze von 1% etwa 48 Stunden. Im Bereich 0,4–4 mg Cu/100 ml folgt die Lichtabsorption streng dem Lambert-Beerschen Gesetz.

EXPERIMENTELLER TEIL

Reagentien

Reagens-Lösung. Polyäthylenimin (200 g 50%ig Wässrige Lösung) werden unter stärkerem Rühren mit Wasser auf 1 l. verdünnt. Von der erhaltenen opaleszierenden Lösung werden 100 ml mit 80–90 ml 2n Salzsäure auf den pH-wert 1–2 eingestellt. Diese Lösung ist mehrere Wochen haltbar. Eine langsam auftretende geringe Trübung kann vor Gebrauch mit einem Faltenfilter abgetrennt werden.

Pufferlösung. Natriumchlorid *p.a.* (200 g), Natriumacetat *p.a.* (50 g) und Eisessig *p.a.* (160 ml) werden in Wasser zu 1 l. gelöst.

Arbeitsvorschrift

Die durch Abdampfen oder Neutralisieren mit Natriumhydroxid von grossen Überschüssen an Mineralsäuren befreite salz- oder salpetersaure Probelösung, welche etwa 0,1–1 mg Kupfer in 10 ml enthält, wird im Messkolben von 25 ml Inhalt mit 5 ml Reagenslösung vermischt, und sofern noch keine intensivere Blaufärbung aufgetreten ist, mit kleinen Anteilen gesättigter Natriumacetat-Lösung versetzt. Es soll ein pH-Wert im Bereich 3–6 vorhanden sein. Man fügt dann 5 ml Pufferlösung hinzu, füllt bis zur Marke auf, und photometriert bei 645 mμ in Glasküvetten von 5 cm Schichtlänge mit einem Spektral-, oder auch Filter-Photometer gegen einen Blindansatz der Reagentien.

* Über die Reaktionen der PEI-Carbate und PEI-Nitrosamine, desgleichen über die von PEI-Cellulose und von Cellulose-PEI-Carbat wird berichtet werden.

Spezifität der Farbreaktion

Die Ionen Ni(II), Co(II) und Fe(II) liefern mit PEI schwächere Farbreaktionen bei anderen Lagen für λ_{max}. In der Arbeitsweise gemäss vorstehender Vorschrift werden bei der Bestimmung von 500 μg Cu(II) folgende Spezifitäten erreicht:

Cu(II)	Ca(II)	Mg(II)	Fe(II)	Al(III)	Fe(III)	Co(II)	Ni(II)	Zn(II)	Mn(II)
1	800	5000	15	100	2	10	3	50	1000

Anwendbarkeit des Verfahrens

In in Königwasser gelösten Legierungen kann nach Abfiltrieren der Kieselsäure und Puffern auf pH 3–5 der Kupfer-Gehalt unmittelbar bestimmt werden, wie die Untersuchung folgender Legierungen zeigt:

	Si %	Mg %	Fe %	Ni %	Mn %	Ti %	Zn %	Cr %	Haupt Bestandteil	Cu gegeben %	Cu gefunden %
Gegeben	0,28	1,57	0,4	2,0	—	0,013	—	—	Al	4,16	4,15
Gegeben	0,23	2,6	0,28	—	0,2	—	5,1	0,17	Al	1,25	1,27

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Zusammenfassung—Mit Polyäthylenimin können in Leichtmetall-Legierungen Kupfer-Gehalte von 0,3–10% bei 645 mμ photometrisch bestimmt werden. Reaktionen der Polyimine mit HNO_2, CS_2, HgJ_2, As_2S_3 werden aufgezeigt.

Summary—Copper (0·3–10%) in light metal alloys can be determined spectrophotometrically at 645 mμ by means of the colour produced with polyethylene imines. The reactions of these reagents with HNO_2, CS_2, HgI_2 and As_2S_3 have also been investigated.

Résumé—On peut doser spectrophotométriquement le cuivre (0,3–10%) dans des alliages métalliques légers à 645 mμ au moyen de la coloration produite avec les polyéthylène imines. On a aussi étudié les réactions de ces réactifs avec HNO_2, CS_2, HgI_2 et As_2S_3.

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Synthesis and analytical applications of 2,4-dinitro-6-chlorophenylazothymol

(*Received* 12 *July* 1966. *Accepted* 18 *December* 1966)

VARIOUS azo-dyes,[1-5] anthraquinone dyes,[6-8] and Thiazole Yellow,[9] have been used as sensitive reagents for the spot detection of magnesium, but certain cations interfere in these tests. The compound 2,4-dinitro-6-chlorophenylazothymol (MS) has been found to be not only a suitable spot-test reagent for magnesium but also a useful acid–base indicator.

EXPERIMENTAL

Synthesis of MS

To a solution of 2,4-dinitro-6-chlorophenylhydrazine[10] (2·3 g) in alcohol (*ca.* 10 ml) add a solution of thymoquinone[11] (1·6 g) in alcohol (8 ml). Heat the mixture under reflux on a boiling water-bath for 30 min. Cool the mixture and add 30 ml of distilled water. Scrape the sides of the reaction vessel to produce a red amorphous compound (yield 3 g), filter it off, wash it with water, and dry it. The compound does not appear to be amenable to crystallization, but the analytical results for it are satisfactory. (Found: C 50·5%; H 3·8%; Cl 9·3%; N 14·6: $C_{16}H_{15}ClN_4O_8$ requires C 50·72%; H 3·96%; Cl 9·37%; N 14·79%: m.p. 183°.)

Spot-test for magnesium

On a spot-plate. Mix one drop (0·05 ml) of the magnesium test solution on a porcelain spot-plate with one drop of 0·01 *M* sodium hydroxide, and one drop of $10^{-3}M$ alcoholic solution of MS. A blue precipitate indicates a positive test. The limit of identification is 0·14 μg of magnesium in 0·05 ml, and the dilution limit is 1:350,000.

On a test-paper. Dip filter paper (Whatman No. 1) into 0·01*M* sodium hydroxide and then into $10^{-3}M$ alcoholic solution of MS, and dry it. The dry paper is pale blue. Add a drop of the test solution to the paper. Magnesium reacts immediately to give a blue spot. The sensitivity is 0·12 μg of magnesium.

Interferences

Oxalate, tartrate, acetate, borate, phosphate, chloride and bromide did not interfere in the test. Several cations were tested for interference and the maximum amounts of them that could be tolerated in 1 drop of test solution are shown in Table I. Silver gave a buff colour and manganese(II) gave a

TABLE I.—TOLERANCE OF INTERFERING CATIONS*

Cation	Amount tolerated, μg	Cation	Amount tolerated, μg
Be^{2+}	24	Sn^{2+}	32
Ca^{2+}	22	Sn^{4+}	32
Fe^{3+}	19	Cu^{1+}	29
Fe^{2+}	18	Cu^{2+}	28
Cd^{2+}	36	Ce^{4+}	1
Cr^{3+}	28	V^{4+}	0·9
Ni^{2+}	10	U^{4+}	0·9
Zn^{2+}	11	Co^{2+}	10
Ba^{2+}	20	Al^{3+}	18
Ag^{+}	0·6	Mn^{2+}	0·4

* 0·5 μg of Mg^{+2} was taken for each test.

dark brown, but ammonium ions made both colours rather blue. Silver can be masked by addition of cyanide, and manganese by oxidation with periodate.

TABLE II.—ACID DISSOCIATION CONSTANTS OF (MS) AT 0·01M AND 27°C

pH	Absorbance	pK_a
7·18	0·042*	—
7·65	0·105	8·29
7·94	0·143	8·31
8·08	0·159	8·35
8·20	0·183	8·34
8·46	0·235	8·33
8·72	0·277	8·35
10·53	0·377†	—
	Mean pK_a	8·33

* Absorbance when the compound was in completely molecular form.
† Absorbance when the compound was in completely dissociated form.

Choice of reaction conditions

An alcoholic solution of the dye was deep red; in alkaline medium it was blue-violet. The sharpest development of the deep blue colour formed between magnesium hydroxide and the dye occurred in the pH range 10·5–11·6. At a pH lower than 10·5 no colour change appeared.

When the amount of magnesium was varied from 1·2 down to 0·11 μg, it was found that with less than 0·14 μg of magnesium the precipitate developed a green colour instead of blue. When the amount of magnesium was kept constant at 0·14 μg and that of the dye was varied, it was found that the best colour adsorption on the precipitate could be achieved when 0·05 ml of $10^{-3}M$ alcoholic solution of the dye was used.

Spectrophotometric determination of the acid dissociation constant of the dyestuff

The pK_a value was determined by Robinson's method.[12] The concentration of the dye was kept at 0·01M throughout, and precipitation of the dye during dilution with water was prevented by addition of alcohol. The results are given in Table II. The compound is yellow in acidic and sky-blue

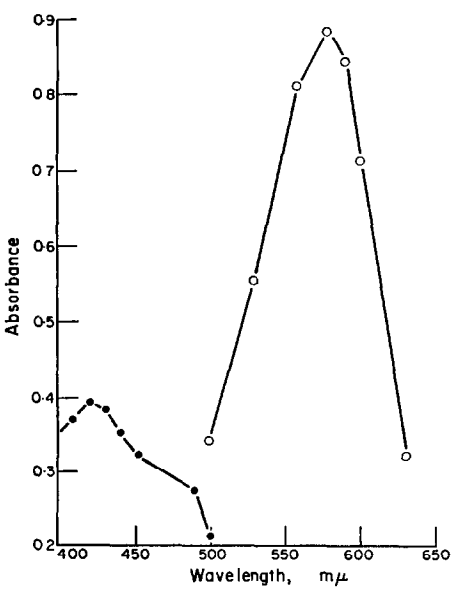


FIG. 1.—Absorption spectra of MS.
●—Acidic medium; ○—alkaline medium.

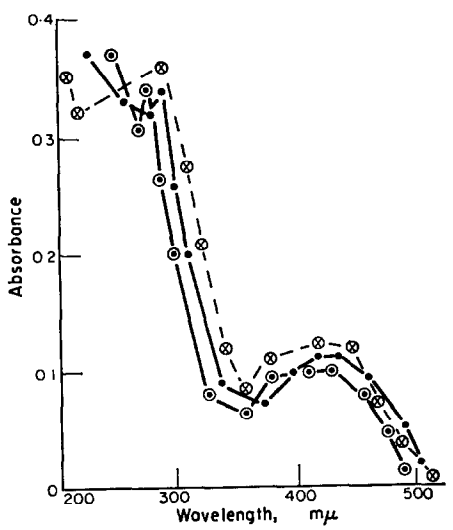


FIG. 2.—Absorption spectra of MS in various solvents (2 ppm solution).
●—Alcohol; ⊙—benzene; ⊕—hexane.

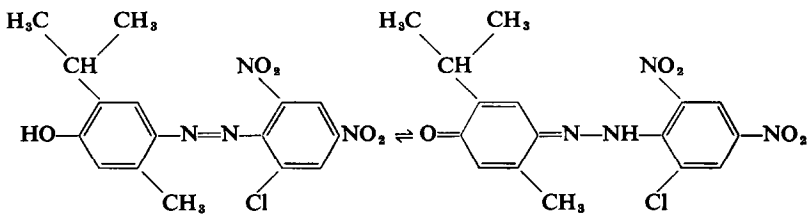
in alkaline media, and exhibits halochroism when dissolved in conc. sulphuric acid. The absorption spectra of the two forms are shown in Fig. 1. Its transition interval is from pH 7 to pH 9.

Use of the dye as an indicator

The reagent was tested as an indicator for the titration of 1, 0·02, and 0·001 *M* solutions of hydrochloric, nitric, and acetic acids with alkali of corresponding concentration. The relative standard deviation for a 50-ml titration ranged from 0·04 to 0·20% for hydrochloric and acetic acids, depending on their concentration, but was higher (0·2–0·3%) for all concentrations of nitric acid. The compound is not very suitable as an indicator for titrations of acids or bases more dilute than $10^{-3}M$, as the indicator then loses its colour near the equivalence point, though the colour is restored on further addition of acid or alkali.

DISCUSSION

The condensation product gave similar absorption spectra irrespective of the solvent (Fig. 2). Although it behaves predominantly as an azophenol it exhibits tautomeric behaviour as a mono-phenylhydrazone of thymoquinone.



Thus it not only forms a sodium salt and an acetyl derivative (like phenolic compounds) but also a dihydrazone with phenylhydrazine (like quinonoid compounds).

MS obtained by the condensation of thymoquinone and the substituted hydrazine was found (by means of a mixed m.p. determination and from the absorption spectra) to be identical with the compound formed by coupling the diazonium salt of 2,4-dinitro-6-chloroaniline with thymol, indicating that its structure is 2,4-dinitro-6-chlorophenylazothymol.

The production of the blue lake probably involved chemi-adsorption of the dyestuff on magnesium hydroxide, since no simple stoichiometry was found for the reaction. The dye anion may be bound on the surface of magnesium hydroxide gel particles, the magnesium ions in the surface of the gel binding the azothymol:

$$[Mg(OH)_2]_x + H\cdot Az\cdot Th \rightarrow [Mg(OH)_2]_{(x-1)}\cdot Mg\begin{matrix}Az\cdot Th\\ \diagup\\ \diagdown\\ OH\end{matrix} + H_2O$$

$$[Mg(OH)_2]_x + Az\cdot Th^- \rightarrow [Mg(OH)_2]_{(x-1)}\cdot Mg\begin{matrix}Az\cdot Th\\ \diagup\\ \diagdown\\ OH\end{matrix} + OH^-$$

That a bluish violet alkaline solution of the dyestuff was taken up by pure filter paper free from magnesium to give a sky-blue colour also supported the fact that the colour change was due to adsorption and not to compound formation.

Acknowledgements—The authors are grateful to the late Dr. D. S. Deorha for suggesting the work, and to Dr. R. C. Mehrotra, Professor and Head of the Chemistry Department for providing the necessary facilities.

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Summary—The newly synthesized 2,4-dinitro-6-chlorophenylazothymol, a weak acid with pK_a 8·33 ± 0·04 at 27°, is proposed as a sensitive spot reagent for magnesium, with an identification limit of 0·14 μg at pH 10·5–11·6. Silver and manganese(II) interfere but can be masked by means of cyanide and periodate respectively. There is little interference by anions. The reagent also serves as an acid–base indicator with a transition interval of pH 7–9, giving a sharp colour change at the equivalence point.

Zusammenfassung—Das neu dargestellte 2,4-Dinitro-6-chlorphenylazothymol, eine schwache Säure mit pK_a = 8,33 ± 0,04 bei 27°, wird als empfindliches Tüpfelreagens auf Magnesium vorgeschlagen; die Nachweisgrenze ist 0,14 μg bei pH 10,5–11,6. Silber und Mangan(II) stören, können jedoch mit Cyanid bzw. Perjodat maskiert werden. Anionen stören wenig. Das Reagens dient auch als Säure–Basen-Indikator mit Umschlagsbereich bei pH 7–9; der Farbumschlag am Äquivalenzpunkt ist scharf.

Résumé—On propose le 2,4-dinitro 6-chlorophénylazothymol nouvellement synthétisé, qui est un acide faible avec pK_a = 8,33 ± 0,04 à 27°, comme réactif à la touche sensible du magnésium, avec une limite d'identification de 0,14 μg à pH 10,5–11,6. L'argent et le manganèse-(II) interfèrent mais peuvent être dissimulés au moyen de cyanure et de periodate respectivement. Il y a peu d'interférences du fait des anions. Le réactif sert aussi comme indicateur acide–base avec un intervalle de transition de pH 7 à 9, offrant un changement de coloration net au point d'élquivalence.

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Studies on metallochromic indicators—I

Pyrocatecholphthalein as metallochromic indicator

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ALTHOUGH a number of phthalein[1] and sulphonphthalein[2,3] dyes have been used as metallochromic indicators, the metallochromic behaviour of pyrocatecholphthalein (PCP) has not been reported. Patrovský[4] used it for the photometric determination of boron, and mentioned the possibility of its being used as an indicator for metals. In the present studies, the indicator properties of PCP have been investigated, and the dye has been found useful in titrations of a number of metals with EDTA, both in alkaline and in slightly acidic medium. Thorium and bismuth(III) may be titrated in the pH ranges 2·5–3·5 and 2–3 respectively, the buffer used being a mixture of sodium acetate and nitric acid. In alkaline medium, copper(II), nickel, cobalt(II), manganese(II) and lead(II) may be titrated at pH 9–9·5, magnesium, cadmium and zinc at pH 10–10·5 in ammonia–ammonium chloride buffer, and calcium at pH 12 in the presence of sodium hydroxide. Further, calcium, strontium and barium can be titrated in an ammoniacal buffer at pH 10 with added magnesium–EDTA complex, using this indicator. It has been found that in alkaline medium, sharper end-points are obtained with this indicator than with Pyrocatechol Violet (PCV).

EXPERIMENTAL

Synthesis of pyrocatecholphthalein

Patrovský's method was used[4] and also the following method, which gave better yields. Pyrocatechol (22 g), phthalic anhydride (15 g), and concentrated sulphuric acid (2 ml) were heated on an oil-bath at 120–130° until the melt became viscous (about 30–35 min). The melt was dropped into 250 ml of water which was then boiled, cooled and filtered. Upon further cooling with ice, a viscous black product precipitated. This was separated and dissolved in dilute sodium hydroxide solution; on addition of dilute hydrochloric acid a greenish black precipitate was obtained and filtered off. It was dried in air and recrystallized from ethanol; yield 19·5 g.

Reagents

EDTA solutions were prepared from the disodium salt, analytical reagent grade (B.D.H.).[6]

Metal ion solutions were prepared from analytical reagent grade salts.

Buffer solutions of the required pH values were prepared[6] and their pH was checked with a Cambridge pH meter.

Spectral characteristics

The absorption spectra of PCP at various pH values were determined with the Beckman model DU spectrophotometer, and are shown in Fig. 1. The absorption maximum at high pH occurs at 595 mμ.

Direct titrations in acidic medium

Solutions containing not more than 1·0 mg of thorium or 0·5 mg of bismuth per ml were mixed with equal volumes of the acetate buffer solution at pH 2·5–3·5 or 2–3 respectively. Two drops of 0·2% ethanolic solution of the indicator were added for each 10 ml of solution, giving a green colour. The solution was titrated with standard EDTA solution till the colour changed abruptly to pale yellow.

Direct titrations in alkaline medium

Solutions of the appropriate metal ion (0·05, 0·01 or 0·001 *M*) were mixed with equal volumes of ammoniacal buffer solution, and two drops of a 0·1% indicator solution were added. The greenish blue solution was titrated with EDTA solution till the colour changed to reddish violet. For the titration of calcium, strontium or barium, 1 ml of 0·01 *M* solution of the magnesium–EDTA complex was added before titrating. Calcium was also titrated in the presence of 0·01 *M* sodium hydroxide.

RESULTS AND DISCUSSION

Pyrocatecholphthalein in aqueous solution is yellow below pH 5, reddish violet above pH 8, and

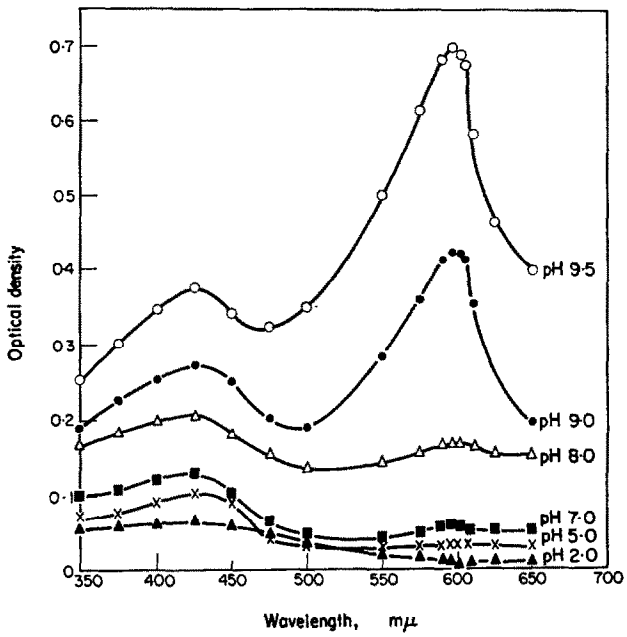

FIG. 1.—Absorption spectra of pyrocatecholphthalein at varied pH.

green between pH 5 and 8. Above pH 8 it forms greenish blue complexes with various bivalent metal ions *e.g.*, magnesium, zinc, manganese, lead, cobalt, nickel, copper, and cadmium. The colour change at the end-point in EDTA titrations is from greenish blue to reddish violet, and is very sharp and reversible. Calcium, strontium and barium do not form green complexes with the dye in ammoniacal medium, but can be titrated in the presence of the magnesium–EDTA complex, in which case the end-point is indicated by the change of the colour of the magnesium–dye complex to that of the free dye. In the absence of the ammoniacal medium, but in dilute sodium hydroxide solution, calcium gives a green colour with the dye, and may be titrated directly with EDTA. Barium and strontium do not show this behaviour and cannot be titrated.

At lower pH values (2–4) the dye forms green complexes with thorium, bismuth, iron(III), zirconium, gallium, indium and aluminium, the free indicator being yellow. However, only thorium and bismuth can be titrated with EDTA with this indicator (colour change from green to pale yellow) as the other metal ions give a slow, gradual colour change at the end-point.

TABLE I.—TITRATIONS WITH EDTA AND PCV OR PCP AS INDICATOR

Metal ion	Concentration, *M*	Volume of EDTA,* *ml*	
		PCV	PCP
Zn^{2+} Mg^{2+} Cu^{2+}	0·05	9·99–10·01	9·99–10·01
Ni^{2+} or Cd^{2+}	0·01	9·98–10·03	9·99–10·02
Zn^{2+}	0·001	9·91–10·12	9·95–10·06
Mg^{2+}	0·001	9·90–10·12	9·95–10·07
Cu^{2+}	0·001	9·92–10·10	9·96–10·04
Ni^{2+}	0·001	9·98–10·14	9·94–10·06
Cd^{2+}	0·001	9·91–10·13	9·96–10·05

* The EDTA solutions were of the same molarity as the metal to be determined. The spread of results was that obtained from six titrations for each metal.

A comparison of the indicator properties in alkaline medium shows the superiority of PCP over PCV. The colour change with the former is from greenish blue to reddish violet which is more easily observed than the blue to violet one in the case of PCV.[5] Not only does PCP give a better colour change than PCV, because of the greater spectral shift, but it is slightly more stable in alkaline solution. Moreover, this indicator is found suitable in the titration of lead in ammoniacal buffer, using tartrate as auxiliary complexing agent, under which conditions PCV gives an indistinct colour change at the end-point. However, at lower pH values, PCV is a superior indicator. The sulphonic acid group on PCV is a stronger acid than the carboxylic acid group on PCP. In Table I are summarized the results of titrations done with the two indicators, showing the spread of results at different concentrations of the metal ions. From these data it is evident that PCP is superior in alkaline solution.

Pyrocatecholphthalein is a better indicator than pyrocatecholviolet for EDTA titrations of several metal ions in alkaline medium, because of its sharper colour change at the end-point. It is also cheap and easy to synthesize.

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Summary—Pyrocatecholphthalein has been used as a metallochromic indicator for the direct complexometric titrations of a number of metal ions with EDTA, both in acidic and in alkaline medium. Th, Bi(III), Ba, Sr, Ca, Mg, Mn(II), Pb(II), Cu(II), Cd, Ni, Co(II) and Zn have been successfully titrated. In comparison with Pyrocatechol Violet, this dyestuff gives sharper end-points when the titrations are done at high pH.

Zusammenfassung—Brenzcatechinphthalein wirde als Metallfarbindikator zu direkten komplexometrischen Titrationen einer Anzahl von Metallionen mit EDTA in saurem und alkalischem Medium verwendet. Th, Bi(III), Ba, Sr, Ca, Mg, Mn(II), Pb(II), Cu(II), Cd, Ni, Co(II) und Zn wurden mit Erfolg titriert. Verglichen mit Brenzcatechinviolett gibt dieser Farbstoff schärfere Endpunkte, wenn die Titrationen bei hohem pH ausgeführt werden.

Résumé—On a utilisé la pyrocatécholphtaléine comme indicateur métallochrome pour les dosages complexométriques directs d'un certain nombre d'ions métalliques au moyen d'EDTA en milieu tant acide qu'alcalin. Th, Bi(III), Ba, Sr, Ca, Mg, Mn(II), Pb(II), Cu(II), Cd, Ni, Co(II) et Zn ont été dosés avec succès. Par comparaison au violet de pyrocatéchol, ce colorant donne des points de fin de dosage plus nets lorsque les dosages sont menés à pH élevé.

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Interference of the ammonium ion in Mohr's method for the determination of chloride

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THE ammonium ion has never been regarded as interfering in the Mohr method for chloride as long as an appropriate pH is maintained. Kolthoff and Stenger[1] state "In the presence of ammonium salts a pH between 6·5 and 7·2 should be maintained". Belcher, Macdonald and Parry[2] concur: "It is well-known that when ammonium salts are present the pH should not exceed 7·2, otherwise the end-point comes too late . . . " A standard text[3] even recommends the use of ammonia solution and ammonium acetate for the neutralization of mineral acids prior to the titration.

We used ammonia solution for pH adjustment of acidic chloride solutions and obtained high results. We decided to investigate this by titrating standard sodium chloride solutions in the presence of weighed quantities of ammonium nitrate and ammonium sulphate.

EXPERIMENTAL

Reagents

Analytical reagent-grade chemicals were used throughout.

A stock sodium chloride solution was prepared by dissolving 5·0021 g of sodium chloride in distilled water, and diluting to the mark in a 1-litre volumetric flask.

A 0·1*M* silver nitrate solution was prepared and standardized against aliquots of the sodium chloride solution.

The mixed chromate-dichromate indicator recommended by Belcher *et al.*[2] was used.

A 0·02*M* sodium hydroxide solution was used for pH adjustment.

A Beckman Zeromatic II pH meter was used for pH measurement.

Procedure

Aliquots (10 ml) of the stock chloride solution were taken for analysis and diluted to 60 ml with distilled water. A weighed amount of ammonium nitrate was added and the pH was adjusted with sodium hydroxide solution. Then 20 drops of the mixed indicator were added, and the sample was titrated with the standard silver nitrate solution.

RESULTS AND DISCUSSION

The results are summarized in the Table I.

TABLE I.—TITRATION OF CHLORIDE IN THE PRESENCE OF THE AMMONIUM ION

NH_4^+ salt added, *g*		Final pH	Cl^- taken, *mg*	Cl^- found, *mg*	Error, %
NH_4NO_3	0·10	6·75	30·4	30·4	0·0
NH_4NO_3	0·30	6·79	30·4	30·5	+0·3
NH_4NO_3	0·60	6·72	30·4	30·7	+1·0
NH_4NO_3	1·00	6·61	30·4	30·9	+1·7
NH_4NO_3	1·50	6·61	30·4	31·3	+3·0
NH_4NO_3	2·00	6·60	30·4	31·4	+3·3
$(NH_4)_2SO_4$	1·65	6·62	30·4	31·4	+3·3

From these results, we feel that the presence of more than 100 mg of ammonium ion cannot be tolerated for quantitative work. If the ammonium ion is present, we recommend it be removed by the addition of sodium hydroxide and boiling and that the pH subsequently be readjusted.

We believe that the probable cause of the interference is the removal of free silver ion from the

solution through the formation of stable silver-ammonia complexes. The removal of free chromate from solution by the equilibrium reaction

$$NH_4^+ + CrO_4^{-2} = NH_3 + HCrO_4^-$$

is also possible.

Acknowledgement—This work was performed in support of a contract (14-01-0001-1114) from the Office of Saline Water, Department of the Interior.

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Summary—The ammonium ion has been found to interfere in the Mohr method for the determination of chloride.

Zusammenfassung—Es wurde gefunden daß das Ammonium-Ion bei der Chloridbestimmung nach Mohr stört.

Résumé—On a trouvé que l'ion ammonium interfère dans la méthode de Mohr pour le dosage du chlorure.

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LETTER TO THE EDITOR

Thorium-free ammonium hexanitratocerate

SIR,

There is considerable interest in the provision of pure chemicals and in the assessment of the impurities present in them. We have recently modified the Smith, Sullivan and Frank preparation and purification of ammonium hexanitratocerate,[1] and have assessed different methods of determining the thorium content of the product. It is difficult to remove the thorium because of isomorphism, and multiple recrystallization is required to remove it completely.

Bastnaesite, a thorium-free cerium fluocarbonate, $CeFCO_3$, from deposits at Mountain Pass, California (Molybdenum Corporation of America) is commercially available. Its conversion into ammonium hexanitratocerate seems rather complicated. Hydrated cerium dioxide, low in thorium content, obtained from monazite sand after separation of the thorium, is also commercially available. The preparation of ammonium hexanitratocerate from this raw material has been described by Smith, Sullivan and Frank,[1] and by Smith and Fly,[2] and the product is now commercially available[3] in reference-purity quality.

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Spectroscopic analysis indicated that the starting supply of commercially available nitratocerate[3] contained not more than 50 ppm of thorium, whereas chemical analysis showed the presence of only 5 ppm of thorium.

The ammonium hexanitratocerate (200 g) was dissolved in 150 ml of hot water. Enough hydrated thorium nitrate was then added to give a Th to Ce ratio of 1:60. The temperature was raised to 100° and 200 ml of 67% nitric acid were added at the rate of 15–20 ml/min with constant heating and stirring. The heating was stopped and stirring continued until the mixture had reached room temperature.

The nitratocerate thus recrystallized was filtered off with the equipment previously described[4] and centrifuged at 2000 rpm for 10 min at an average distance of 17·5 cm from the centre of rotation: yield 70–75%. The product obtained was drenched by addition of 25 ml of reagent-grade nitric acid and centrifuged for 10 min: this treatment was then repeated and the product was called the first crop. It was dried at 85° and part of it was set aside for analytical determination of its thorium content.

This recrystallization process was repeated, with proportionate diminution of the volumes of solution and nitric acid, to obtain the second, third and fourth crops of crystals, which were then evaluated for their co-precipitated thorium content by spectroscopic, neutron-activation, and chemical procedures. Recognized experts in their various fields of specialization were commissioned to carry out referee analyses. The results are shown in Table 1.

TABLE 1

	Thorium, *ppm*			
	Analyst 1*	Analyst 2*	Analyst 3†	Analyst 4‡
Starting material	50	50	125	5
1st Crop	1240	1250	1490	—
2nd Crop	415	460	506	—
3rd Crop	110	140	226	—
4th Crop	40	50	129	87

* Analysis by emission spectroscopy.
† Analysis by activation analysis.
‡ Analysis by extraction and spectrophotometry.

It is noteworthy that the independent spectroscopic analyses agreed better with each other than with the other analyses, and it is evident that considerable research remains to be done on comparison of methods of trace analysis and selection of referee methods.

As expected, the amount of thorium left in ammonium hexanitratocerate on recrystallization is governed by the original thorium content. The best method of obtaining thorium-free hexanitratocerate appears to be to start with hydrated cerium dioxide, dissolve it in nitric acid, and precipitate the desired product by adding ammonium nitrate. By this means lower yields are obtained, but the product is certainly less contaminated by thorium from the raw material. Hydrated cerium dioxide, sufficiently low in thorium content for the hexanitratocerate obtained from it to need no recrystallization to be equal in quality to the fourth crop quoted above, is commercially available in quantity, and therefore so is ammonium hexanitratocerate of the quality needed for radiochemically pure cerium.[5] The results reported here confirm those previously reported,[5] and show that this is probably the best method of preparing a cerium(IV) salt with minimal thorium content.

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24 February 1967

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TALANTA REVIEW*

A CRITICAL REVIEW OF METHODS OF ISOLATING AND SEPARATING THE NOBLE METALS—III†

CHROMATOGRAPHY, PRECIPITATION AND FIRE ASSAY

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Summary—This review deals with the chromatographic, precipitation and fire-assay methods of separating the seven noble metals, published subsequent to the previous reviews and prior to January 1966. The noble metal species present in solution are discussed in so far as they relate to separation and determination.

THIS paper continues the review of recent methods of separating and isolating the noble metals, and the prologue to Part II† applies equally to Part III.

PAPER CHROMATOGRAPHY

The platinum metal complexes with tin(II) chloride and bromide were used by Lederer and Shukla[1] for a number of separations by paper chromatography: 1 ml of aqueous solution containing 1 mg of each of the six metals was mixed with 1 ml of 1*M* tin(II) chloride in hydrochloric acid. Ascending development was used with the metal solution applied as a thin band. The solvent was 1*M* tin(II) chloride in 6*M* hydrochloric acid. Investigation was made of the effects on the R_f values when the hydrochloric acid and tin(II) chloride concentrations in the solvent were varied. The separation of platinum and palladium was better than that achieved by partition chromatography of the chloro-complexes. The spots were well defined, showing for platinum an orange colour and an R_f value 0·21, and for palladium a blue colour with R_f 0·70. For rhodium the spot was elongated with a red front and a yellow rear and an R_f spread from 0·13 to 0·56. Heating the solutions of the metal complexes had little effect on the chromatographic behaviour. Iridium formed two yellow-brown spots with R_f values of 0·18 and 0·78. Mixtures of ruthenium–palladium, osmium, ruthenium, platinum–palladium and platinum rhodium–palladium as the tin(II) bromide complexes in 3*M* hydrobromic acid were successfully separated with the solvent 0·5*M* tin(II) bromide in 3*M* hydrobromic acid. In the case of potassium chloroiridate(VI) dissolved in water or boiled with hydrobromic acid there were three spots, one red and two yellow with R_f values 0·19, 0·32, 0·87. If iridium(IV) was first heated with tin(II) bromide–hydrobromic acid mixture, four spots developed, one red and three yellow with R_f values 0·23, 0·37, 0·65 and 0·88. No explanation was offered for this phenomenon. The authors suggested that the complexes were similar in structure to heteropolyacids with the metal as the central atom surrounded by four or more tin chloro-complex groups. It was noted that the red tin(II) chloride–rhodium(III) complex could be converted into the yellow form by treatment with hydrochloric acid, by extraction with butanol, or by removing tin(II) during electromigration.

For the detection of gold, platinum, selenium and tellurium Larsen[2] evaporated the chloride solution with nitric acid to eliminate excess of hydrochloric acid, thus ensuring reduction of selenium and tellurium to the quadrivalent state. Ascending development was used with a solvent containing n-butanol, methanol and diethyl ether. The R_f values were: gold, 0·9–1·0: platinum, 0·0: selenium, 0·5: tellurium, 0·0. Platinum was detected with potassium iodide and gold with tin(II) chloride.

* For reprints of this review see advertisement at the front of this issue.
† Part II—*Talanta*, 1967, **14**, 991.

A chromatographic separation of gold, palladium, platinum and ruthenium was described by Vassiliades and Manoussakis.[3] The solvent was isobutanol containing hydrochloric acid to prevent hydrolysis of the metal salts, and acetic acid to encourage clear separation of the zones. A solution of dianisidine hydrochloride was used for locating the zones, the colours and R_f values being; ruthenium, brown-yellow, 0·22: palladium, yellow, 0·51: platinum, dark-yellow, 0·62: gold, brown-red, 0·94. The metal chloride solution contained 150 mg of platinum, 50 mg of palladium, 150 mg of gold and 20 mg of ruthenium per 100 ml. The chromatogram was run for 21 hr at 26°, dried for 2 hr, and then sprayed with the reagent. Continued exposure to air or to hydrogen peroxide modified the colours. For determination of R_f values the solvent front was located by use of ultraviolet light.

A useful series of chromatographic separations for the seven noble metals was described by Blasius and Fischer.[4] Ascending and radial development were both applied and three solvents were used successively, each with some specific advantage. Thiourea was used to locate osmium and ruthenium, and tin(II) chloride and potassium iodide were used for other metals. Iridium was located with concentrated hydrochloric acid, producing a brown zone at the solvent front. Ammonium sulphide was also used for ruthenium. The butanol–hydrochloric acid solvent was recommended for the chloro-complexes of gold, platinum and palladium with either ruthenium or rhodium (the metals are in order of increasing R_f). Sodium nitrite solution was especially useful for the separation of the chloro-complexes of iridium and platinum with or without osmium: the R_f values increased in the order given. Sodium nitrite in ethanol and isopropanol was recommended for separation of the nitrito-complexes of ruthenium and rhodium with either palladium or platinum in nitrite solution. The solvent ethyl methyl ketone–hydrochloric acid was used for the chloro-complexes of rhodium and palladium and the nitroso-chloro-complexes of ruthenium in hydrochloric acid. A variety of combinations of noble metals was separated successfully, and it appeared that osmium and ruthenium could be separated with the butanol–hydrochloric acid solvent: the use of thiourea as locating agent is of special interest. The authors also described a variety of paper ionophoresis separations of the seven noble metals in various combinations. The electrolytes were hydrochloric acid solutions of sodium chloride or acetate; the noble metals were present as the chloro-complexes: potentials of 230 or 130 V were applied for 1 or 2 hr. The variation in bands resulting from sample applications to either the side or centre of the strip and the effect of hydrolysis of platinic acid solution were discussed. Again, there is particular interest in the clean separation of osmium and ruthenium in sodium acetate–hydrochloric acid medium, a potential of 230 V being applied for 1 hr.

For the determination of platinum and palladium James[5] applied the Kember and Wells technique[6] to silver assay beads obtained by the fire-assay of Merensky Reef ores. The bead was parted with nitric acid in a specially designed glass bulb with a closed tail calibrated to contain 1 ml, which allowed control of the evaporation and isolation from the silver chloride formed by treating the parting acid with hydrochloric acid and sodium chlorate solution, the latter ensuring the oxidation of any bivalent platinum: 0·05 ml of the resulting solution was used for the chromatogram. The spotted area was allowed to dry and then inserted into the jar containing the pentanol–hydrochloric acid–hexone solvent and the chromatogram was allowed to develop overnight. The dried strips were sprayed with tin(II) chloride solution, platinum appearing as a yellow band and palladium as a dark purple one. The corresponding areas from a duplicate strip were removed and extracted with 2·5*M* hydrochloric acid for platinum and 0·5*M* hydrochloric acid for palladium. The platinum portion of the stained strip could also be used for the determination. In the filtered extracts platinum was determined with tin(II) chloride and palladium with thioglycollic acid. The results indicate very satisfactory precision. The author stated that "Results obtained with only slight familiarity with the technique compare very favourably with those obtained by laboratories practised in and using standard fire assay methods."

"Capillary chromatography" or, more simply, "spot-testing" has been applied to the separation and detection of rhodium and iridium. Černý and Kubin[7] added an acidified solution of the two metals by capillary to a filter paper impregnated with aluminium hydroxide. Several capillary-loads of water were added to the spot, which was then dried, and sprayed with a solution of tin(II) chloride and potassium iodide. Rhodium appeared as a red ring and iridium as a light brown inner ring. The intensity could be increased by the addition of potassium iodide solution. There was interference from platinum, palladium and gold.

Filter papers impregnated with cadmium sulphide have been used for separation and approximate determination of platinum, palladium, gold, silver and mercury. Ćelap *et al.*[8] claimed that the movement of the products of the metathesis was a linear function of the amount of the ion present. Presumably the precision obtained was 2–5%, depending on the amount of ion present. Some additional evidence for the usefulness of methods such as these might be forthcoming if the technique could be applied successfully to noble metal alloys.

When investigating the paper chromatographic separation of the platinum metals Noddack and Sanir[9] were unable to separate each of the six metals on one chromatogram. The amounts of metals

applied were 20–30 μg and the ascending technique was used. With the solvent ethyl acetate–concentrated hydrochloric acid–acetic acid, the R_f values for ruthenium, rhodium, iridium, palladium, osmium and platinum were respectively 0·10, 0·18, 0·19, 0·42, 0·53 and 0·58. For rhodium and iridium R_f values of 0·49 and 0·88 respectively were obtained with the solvent methyl nitrite–concentrated hydrochloric acid–ethanol. For spot location tin(II) chloride was used for rhodium, palladium and platinum: bromine water for iridium: thiourea for ruthenium: tin(II) chloride with thiourea for osmium.

A potentially useful report on ascending chromatographic separations of the seven noble metals and copper and silver was recorded by Voicu and Nascutiu,[10] who reported the R_f values obtained with eighteen solvents consisting of 1:1 mixtures of various alcohols or ketones with various concentrations of hydrochloric acid. No overall pattern of change of R_f value with increasing acidity appeared. With certain solvents the R_f values decreased with increase in acidity: in several cases the R_f value increased to a maximum with about 4 or 6M hydrochloric acid then decreased at higher acidity: in others the R_f values increased with acidity. A highly acidic ketone–hydrochloric acid solvent separated a large and more varied number of metals. The C_1–C_3 alcohols showed maxima in the R_f values. The C_4–C_5 alcohols provided relatively varied separations. Detailed examination of the tables suggests a variety of chromatographic separations of noble metals which are frequently associated as groups in analytical separations or as predominant groups in natural deposits. In general, the solvents allowed good separations of gold and platinum or gold and palladium. On the other hand, with solutions of platinum and palladium in 1M acid the R_f values indicated considerable separational difficulty for all 18 solvents.

For the chromatographic separation of noble metal groups containing rhodium or platinum with palladium, ruthenium and gold, Kao and Yuan[11] used as solvent oxine dissolved in isobutanol–ethanol–water–acetic acid (60:57:80:3). The metal solutions were buffered at pH 1–2 with dichloroacetic acid.

Thiocyanate in hydrochloric acid solution was used as locating agent and ethyl methyl ketone as solvent to separate the platinum metals into the groups: iridium, rhodium–ruthenium, platinum–palladium and osmium. In a second method Kao and Sun[12] used benzene saturated with thiocyanate as the solvent and hydrochloric acid, potassium chloride and thiocyanate as locating agent. Gold, palladium and platinum–ruthenium–rhodium–iridium could be separated. The authors are continuing their work with a view to separating iridium from rhodium.

Filter paper impregnated with butyl phosphate was used by Hu and Shi[13] to separate the groups gold–platinum–palladium–rhodium and osmium–palladium–rhodium by reverse-phase paper chromatography. Hydrochloric acid was used as solvent, and increasing its concentration had little effect on the R_f values, which for gold, platinum, palladium, and rhodium were 0, 0·2, 0·4–0·6 and 0·9 respectively. With 2–10M hydrochloric acid, gold remained at the origin. With $>8M$ hydrochloric acid, silver migrated as $AgCl_3^-$. With $>2M$ hydrochloric acid selenium and tellurium could be separated. In a second paper Hu and Shi[14] added variations to the method. Mixtures of gold or silver with platinum–palladium–rhodium could be separated with hydrochloric acid that was $<6M$. The R_f value of palladium increased with increased acid concentration. With nitric acid as solvent the R_f values of rhodium, selenium, tellurium, silver and gold changed very little with increased concentration of acid while there was a slight increase in the case of ruthenium, palladium, osmium and platinum. Unfortunately the chromatographic behaviour of iridium was not indicated. The persistently high R_f value of about 0·93 for rhodium indicates a clear separation from the remaining noble metals.

Kertes and Beck[15] used ammonium thiocyanate and nitric acid solutions of some sixty ions including gold and platinum, and extracted with isoamyl alcohol, methyl isobutyl ether and di-isopropyl ether. The R_f values were recorded for all sixty ion species. The use of thiocyanic acid in paper partition chromatography was also discussed by Locke and Martin,[16] who determined the chromatographic properties of eight solvents. Of the noble metals, only gold was included among the 38 ions used. The solvents were n-butanol–water–perchloric acid and seven complexing solvents based on an n-butanol–water–thiocyanic acid mixture to which was added pyridine, aniline or quinoline. The authors discussed criteria of complexing properties.

For the analysis of platinum metals, Kao and Chang[17] used two solvents, n-amyl methyl ketone–hydrochloric acid and acetone–hydrochloric acid–acetophenone. Both solvents provided speed and stability. The locating reagents were tin(II) chloride for gold, platinum–palladium, rhodium and ruthenium: thiourea for osmium: chlorine water for iridium. With the first solvent the chromatogram was run for 1 hr at room temperature, for the other 3 hr at 9·5–10° was required. With both solvents silver remained at the start and the osmium spots were scattered. The acetone solvent could be used to separate rhodium from iridium. Large amounts of sulphate, nitrate, chloride, phosphate and perchlorate did not interfere. Perchlorate concentrated the platinum spots with the acetone solvent. The method was applied to determine gold in electrolytic slimes following the isolation of gold by hydrogen peroxide.

Variations in chromatographic methods are being proposed, some of which offer useful adaptations to analytical areas of wide interest. Photographic emulsions have been used in many methods to detect the presence of gold in solid materials. The autoradiographic plate was used by Shima[18] to trace the losses of radioactive gold to pot wall, cupel *etc.* during a fire assay. The technique involved cutting the used pot or cupel into two equal parts. The extent of the penetration of gold, and thus of the losses, was determined by pressing the thin vinyl membrane against the freshly cut areas for 3 days and then developing and fixing as usual. The results obtained were discussed in a recent review.[19]

To detect *in situ* the presence of gold minerals, Rao and Sagar[20] used gelatine-coated paper strips impregnated with *aqua regia* and pressed the paper against a surface of polished mineral sections for 20–30 sec. The paper was removed and treated with pyridine in hydrobromic acid. In the presence of gold, cherry-red spots appeared. Presumably, the associated constituents in minerals do not interfere. Photographic paper washed free from silver by thiosulphate and water may be used as the paper base.

A similar method for the detection of gold in ores was reported by Lever[21] some years earlier. The ore and paper were pressed between two glass plates and the gold was extracted by *aqua regia* onto the paper, treated with ethyl acetate–nitrate acid mixture and finally identified with tin(II) chloride. Applied to ores containing 0·05–0·15 troy oz of gold per ton the method gave uncertain results with some interference from iron. The author reported a more satisfactory semi-quantitative chromatographic method for estimating gold in the range from 25 to 250 μg per assay ton of ore. Six samples can be examined in 2 hr and the range of application can be extended by simple modifications. For siliceous ores a 100-mesh sample weighing 1·5 g was treated with *aqua regia* and the mixture was heated and filtered. Orthophosphoric acid was added to complex iron, and gold was extracted with ethyl acetate. The aqueous phase was removed and potassium chlorate added to the organic phase to remove residual water. The organic phase was transferred to chromatographic strips (pretreated with potassium chlorate solution) over an area previously marked between 1 and 5 in. from one end. The strip was dried and the end nearest the 1-in. mark was immersed in the developing solution (methanol–hydrobromic acid–potassium chlorate). When the solvent had travelled to the 5-in. mark the strip was removed and air-dried, and the zone at the 5-in. mark was sprayed with tin(II) chloride solution. The intensities of the stains at the 5-in. mark were then compared with standards similarly prepared from a gold solution. The stain could be treated with ammonia fumes to reduce fading. A method for treating sulphide ores was included, in which case potassium chlorate was added before *aqua regia* extraction. The results compared favourably with those of fire assay. Losses of gold in the *aqua regia* and extraction treatments were negligible. The report bears the marks of a carefully considered and precisely executed research project.

Paper chromatography was also used by Agrinier[22] to estimate gold in silicate rocks and minerals. *Aqua regia* extracts, made after roasting the minerals, were evaporated and the residue was taken up in nitric acid. The solvent was ethanol–ethyl acetate–water–nitric acid, and *p*-dimethylaminobenzylidenerhodanine was used as location reagent. R_f values were given for associated base and noble metals: gold appeared at the solvent front. The results for gold compared favourably with those obtained by fire assay.

Thin-layer chromatography was applied by Hranisavljević-Jakovljević *et al.*[23] to separate and then identify gold, with palladium and platinum present as chlorides and silver as acetate. Dithizone extracts in benzene were spotted on silica gel plates and chromatographed with benzene–methylene chloride as solvent. The R_f values and colours were; AgHDz, O, reddish-brown: $Au(HDz)_3$, 0·31, red: Au_2Dz_3, 0·20, lemon-yellow: $Pd(HDz)_2$, 0·43, dark green: $Pt(HDz)_2$, 0·38, yellow. Silver and gold dithizonates were selectively extracted at pH 7·5, palladium at pH 5·5, and platinum at pH 3 after reduction with tin(II) chloride.

Wu and Wu[25] used layers of silica gel mixed with sintered anhydrous calcium sulphate to give faster separation with better-defined spots. With acetone–hydrochloric acid–ethyl acetate or nitric acid–ethyl acetate as solvent separations into four groups were made; gold–osmium, ruthenium–palladium, platinum–rhodium, iridium. With increased proportions of concentrated nitric acid gold–osmium, platinum, ruthenium, palladium, iridium–rhodium could be separated. A potentially useful technique involved fixing the palladium spot at a suitable R_f value by the addition of oxine solution and then using a solvent such as n-butanol saturated with dilute sulphuric acid to separate gold, platinum, and palladium.

Paper electrophoresis was used by Been and Hoeye[26] to determine gold(III) associated with colloidally dispersed gold. Paper strips, wetted with 0·075*M* sodium thiosulphate, were used to provide a clear separation of the ions from the colloidal gold: 5 μl of the samples were streaked in the middle of the strips, and under a constant current of 2·5 mA/cm, the gold(III) ions migrated about 65 mm towards the anode after 1 hr: the gold particles moved 2–5 mm toward the anode. The potential dropped from 400 to 200 V. Gold-198 was used for the determination. For 1–2% of gold(III) the

method showed a deviation of 30% or less from values obtained by paper chromatography: precision was about 10%.

Dithizone[26] has been used for the isolation of platinum and of palladium by chromatography on an alumina column after preliminary extraction of platinum dithizonate from tin(II) chloride–hydrochloric acid solution. Chloroform was used as eluent and 0·2–4 ppm of platinum could be determined. For palladium[27] dithizone separations were made from 1–6*N* hydrochloric or sulphuric acid. Chloroform was again used as eluent. The method could be applied to less than 1 μg of palladium. About 0·01% of palladium could be determined in 1-mg samples of platinum in 30 min. There was no interference from copper, mercury and bismuth.

Ashizawa[28] also separated several new metal dithizonates in a pure state by chromatography with chloroform as the eluent. Absorption maxima were recorded for the dithizonates of cobalt, iron, nickel, palladium, gold, copper and platinum.

Ruthenium and osmium

One of the most useful solutions for the collection of the tetroxides of osmium and ruthenium is cold hydrogen peroxide. Complexing or reducing reagents are sometimes added and determination can be made without the contaminants which are present in such media as sodium hydroxide or sulphite solutions. Koch and Bruchertseifer[29] used paper electrophoresis to characterize the composition of the peroxide solution of the distillates. The tetroxide was distilled from phosphoric acid solution into cooled water. Addition of perchloric acid and hydrogen peroxide gives quantitative formation of ruthenium(IV). With sulphuric acid and hydrogen peroxide ruthenium (III) is formed. To depolymerize the ruthenium(IV) the solution was added to an exchange-resin, Wofatit KPS in the hydrogen form, which was then washed with acidified water and irrigated with perchloric acid.

The effect of aging a solution of $[Ru(H_2O)Cl_5]^{2-}$ in 0·1*M* hydrochloric acid was studied by Shukla,[30] by paper electrophoresis and spectrophotometry. It was shown that aging the complex resulted in gradual hydration involving progressive replacement of the chloro- group by an aquo-group. The absorption spectra of electrophoretically pure $[Ru(H_2O)Cl_5]^{2-}$ and $[Ru(H_2O)_6]^{4+}$ were also reported.

Chromatographic and solvent extraction methods have been described for the separation and determination of the ruthenium constituents in nitric acid solution, specifically in those "aqueous process solutions from chemical separation plants, designed to separate plutonium and fission products from irradiated uranium by solvent extraction." In general, these constituents are of two types, nitrato (non-nitro) and nitro complexes of nitrosylruthenium.[31–33] Fletcher *et al.*[31] suggested graphic formulae for eleven nitrato complexes classified according to the presence or absence of a nitrato group *trans* to the NO-group. Paper chromatograms of ruthenium solutions in 3–15*M* nitric acid, previously aged to reach equilibrium, indicated a division of the complexes into four groups. The R_f values were given for each group with isopropyl methyl ketone (IPMK) and dibutylcellolve (DBC) as solvent.

Brown and Naylor[32] dealing with "process solutions" stated that, in contrast to solvent extractive methods, paper chromatography allowed the characterization and determination of the nitric acid–ruthenium complexes, which were practically all in the stable nitrosylruthenium form and contained the nitrato and the nitro groups. The solvents used were IPMK and DBC, equilibrated with 3*M* nitric acid. With "process solutions" containing mixed fission products, there was some masking of ruthenium by zirconium-95 and niobium-95, which had R_f values of about 0·6. Brown and Naylor[32] determined the ruthenium distribution on the chromatograms by gamma spectrometry. Wain *et al.*[33] used the same solvents with 0·005 ml or less of ruthenium solution applied as a band at the base of the paper. The nitrosylruthenium nitro complexes remain at the start while the nitrato complexes, with a ratio of nitrate to ruthenium greater than 3 to 1 migrate, the R_f values being between 0·2 and 0·7. Points of technique for optimum separation were described and the R_f values for the various nitro and nitrato complexes were included. An empirical formula was given for calculation of the amounts of nitro and nitrate complexes in nitric acid solutions. Scargill and Lyon[34] found anomalous results when the method was applied to uranium solutions. The method indicated "up to 20% of nitro-complexes in solutions known to contain only nitrato-complexes, and also up to 25% of nitrato-complexes in solutions where complete conversion to the nitro-complexes had been obtained." The authors concluded that the Wain method[33] would only give accurate results with the use of a carefully defined technique and in the absence of uranyl nitrate. A revised formula was proposed for general application to irradiated uranium process solutions to determine the proportions of nitrato- and nitro-complexes. The dibutylcellosolve results were used and showed a higher proportion of nitro-complexes in process solutions than that found by the Wain[33] method.

Scargill[35] later provided methods for the separation of individual nitrato and dinitro-complexes of nitrosylruthenium(III) and a method for the determination of the extractable nitrato and dinitro complexes in nitric acid solutions. By reverse-phase chromatography at 0°, with nitric acid as the solvent on paper impregnated with tributyl phosphate, the author was able to obtain 5 groups of

nitrato-complexes, two major groups of nitro-complexes, and to separate mixtures of nitrato- and nitro-complexes into the solvent-extractable nitrato group, the dinitro-complex and the cationic nitro- and nitrato-complexes. By cation-exchange methods he identified the cationic dinitro-complex, $[RuNo(NO_2)_2(H_2O)_3]^+$ and an anionic or neutral complex, $[RuNO(NO_2)_3(NO_3)(H_2O)_2]$. The existence of a mononitro-mononitrato complex was also indicated.

The interesting reaction of osmium(VIII) oxide and potassium iodide, one of the earliest reactions applied volumetrically, was studied chromatographically by Rallo.[36] In hydrochloric acid medium the constituents OsI_6^{2-} and chloroiodo-osmates(IV) were indicated. All of the latter could be converted into the violet OsI_6^{2-} by evaporation on a steam-bath with an excess of iodide. Practically pure OsI_6^{2-} could be obtained by performing the reaction in perchloric acid with sodium iodide.

Rhodium

Electrophoresis and ion-exchange chromatography have been used to identify the dissolved constituents in aqueous acid solutions of rhodium. Shukla and Lederer[37] used paper electrophoresis to determine the conditions for the formation of the yellow and the red rhodium sulphates. In general, a potential of 250 V was applied for 45 min and tin(II) chloride–potassium iodide was used for detection. The authors state that the yellow rhodium sulphate, in which the Rh(III) is cationic can be prepared by dissolving freshly precipitated rhodium(III) hydroxide in *N* sulphuric acid and that in 0·5*N* sulphuric acid several, presumably hydroxo-complex, cations are formed. Heating or evaporating the *N* acid solution results in considerable complexation, yielding a mixture of cationic complexes. Solutions left at room temperature are stable for months. The red rhodium trisulphate could be obtained by heating to 250° but not by heating on the water-bath. In solution it initially forms a single species but on standing tends to form an equilibrium similar to that for aged solutions of the yellow form, with some persistence of the anionic form. The authors[38] also investigated rhodium(III) perchlorate solutions, reaching the conclusion, of some analytical significance, that the single constituent $Rh(H_2O)_6(ClO_4)_3$ could be prepared by precipitating rhodium hydroxide from an aqueous solution of Na_3RhCl_6 with a slight excess of sodium hydroxide, dissolving the precipitate in perchloric acid and re-precipitating until a solution was obtained that had a single absorbance maximum at 396 mμ or gave a single electrophoretic band. Electrophoretic evidence was obtained of the presence of a second constituent of unknown identity in solutions made by boiling chlororhodite with perchloric acid. Previous work by the authors[39,40] indicated that the removal of co-ordinated chlorine from rhodium chloro-salts was not complete in one hydroxide precipitation. This conclusion becomes significant in the analytical separation of rhodium.

Platinum

Paper chromatography has also been applied to separate noble metal complexes in studies of their structural and behavioural characteristics. Thus, Basolo *et al.*[41] separated *cis*- and *trans*-dihalogendiammineplatinum(II) complexes and stated that practically all mixtures of *cis*- and *trans*- as well as of dichloro-, dibromo-, di-iodo-, chloroiodo- and chlorobromo-complexes could be thus separated. Later[42] they made a chromatographic study of platinum metals halides on several resin papers. The R_f values obtained at various hydrochloric acid concentrations indicated that platinum(IV) and platinum(II) could be readily separated. The R_f values for H_2PdCl_4 and H_2PtCl_4 on weak anion-resin and Amberlite SB2 resin papers were closely similar. A cursory examination of platinum chloride solutions containing sulphur dioxide indicated the presence of H_2PtCl_4 and sulphite complexes. Data were provided to confirm the chromatographic separation of chloroammine, amminepyridine and chloropyridine platinum(II) complexes.

Rhodium, iridium, and platinum

Blasius and Preetz[43] used ionophoresis at 3000 V for the separation of aquo and hydroxychloro complexes of rhodium(III), iridium(III) and platinum(IV) in an acetic acid–acetate buffer. Tin(II) chloride was used as location reagent for the ionophoretograms of rhodium(III) and platinum(IV) and chlorine for iridium(III). The authors investigated the temperature dependence of the migration velocity and the effect of aging on the composition of the species. In the case of rhodium, in addition to the main zone, there were a number of intermediate zones which they interpreted to indicate very unstable hydroxy-complexes or higher aggregated ions. The chloroaquo-complexes of rhodium(III) and iridium(III) were isolated and their composition determined by reduction to the metal by zinc and by halogen determination in the filtrate. For rhodium and iridium the cationic zone was characterized by yellow $[MCl_2(H_2O)_4]^+$, the neutral, orange zone by $[MCl_3(H_2O)_3]$ and the anionic zone by rose $[MCl_4(H_2O)_2]^-$ and red $[MCl(H_2O)]^{-2}$.

PRECIPITATION

Gold

Procedures for the extraction of noble metals from ores by dissolution in acids have been described. A number of these methods have been discussed in a review of neutron activation methods.[19] For the determination of gold in sulphide ores, Assarsson *et al.*[44] selectively removed the associated base metals and silver by treatments in a specially designed apparatus with chlorine-free hydrochloric acid. The residue was treated with hydrochloric acid and a little nitric acid to remove the gold, which was finally precipitated by hydrazine sulphate and sodium sulphide in the presence of mercury(II) chloride. The precipitate was ignited, refined by cupellation and weighed. The results, compared with values obtained by fire assay, indicated excellent accuracy.

A method of gold separation from lead and copper concentrates, crude lead, high grade commercial matte and slags was described by Bukharin,[45] for concentrations of over 40 g of gold per ton. A method for silver was included. Initially, the gold and silver were separated by assay melting of the crude lead which was then treated with nitric acid to produce a gold residue. This was heated at 600°, then dissolved in *aqua regia*, and the solution was evaporated in the presence of hydrochloric acid and sodium chloride, then treated with potassium hydrogen fluoride and *o*-dianisidine, and the gold determined volumetrically with hydroquinone. The gold losses were 0·1–0·4%.

For the separation of gold from copper and lead Ujihira[46] precipitated gold from dilute nitric or hydrochloric acid with *p*-dimethylaminobenzylidenerhodamine, 2-mercaptobenzothiazole, thionalide and Methyl Violet. There was interference from iodide, bromide and cyanide.

Palladium

The red-brown precipitate obtained from palladium and Reinecke's salt was used by Voicu and Dema[47] to separate palladium from gold and platinum with reasonable accuracy. The data indicated results for separations from high proportions of rhodium and low values for separations from high proportions of copper, with some significant lack of precision for separations from high proportions of copper, iron, cobalt and nickel. The interferences from various other cations were examined. Recoveries from solutions containing 1–460 μg of palladium were very acceptable. The extractant was ethyl methyl ketone and the medium was 0·1–0·75*M* hydrochloric acid. Large excesses of Reinecke's salt gave more complete extraction.

Ruthenium

As part of an investigation of methods of separating and determining trace amounts of ruthenium, manganese, technetium, rhenium, molybdenum, Jasim *et al.*[48] isolated ruthenium together with manganese by treating the solution with 10% sodium hydroxide solution and heating in a sealed capillary. The centrifuged liquid containing manganese and ruthenium was treated with ammonium sulphide which isolated ruthenium.

The application of co-precipitated iron(III) hydroxide as a collecting reagent for a variety of cations was discussed by Morachevskii *et al.*[49] In the case of ruthenium, ruthenium hexachloride was completely separated at pH 5·4–8·5 whereas in the absence of the iron(III) hydroxide only 76% of the ruthenium was precipitated at pH 7·3 and less at higher pH values.

Palladium, platinum, rhodium and iridium

For the precipitation of palladium and platinum and their collective separation from rhodium and iridium, Ginzburg *et al.*[50] used a suspension of copper(I) chloride in hydrochloric acid that was $\leq 0{\cdot}15M$ and contained 0·5–0·7 g of sodium chloride per 100 ml. The extent to which rhodium was co-precipitated depended on the acidity and the chloride concentration, increasing rapidly with a decrease of sodium chloride concentration below 0·10*M*. Selenium was removed by evaporation from a bromate solution, then tellurium by a cation-exchange (KU-2) separation. The effluent containing platinum, palladium, rhodium and iridium was treated with suspended copper(I) chloride. The mixed precipitate was filtered off and washed with hydrochloric acid at pH 2, then with brine solution to remove the admixed copper chloride. The platinum and palladium were dissolved in *aqua regia* and palladium was determined by dimethylglyoxime and platinum by precipitation with mercury(I) chloride or spectrophotometrically. The filtrate from the copper(I) chloride together with a solution of any residue remaining after dissolution of the platinum and palladium on the filter paper was treated to determine iridium polarographically and rhodium spectrophotometrically. For relatively high rhodium contents, iridium was determined polarographically: a simultaneous precipitation of rhodium and iridium by thiourea was made and rhodium was determined by difference. The data recorded by the authors, all in the milligram ranges, indicated somewhat indifferent separation efficiency and accuracy. Mitigating against the method are factors such as reagent instability, the sensitivity of platinum–rhodium separations to the sodium chloride content, and the adverse effect of high proportions of rhodium.

Rhodium and iridium

For the separation of rhodium from iridium, Tertipis and Beamish[51] heated a 1·0*M* hydrochloric acid solution of the metals to 80–85° in the presence of freshly reduced copper powder. The precipitate of copper and rhodium was collected and treated with *aqua regia*, and any residue was chlorinated at 700° in the presence of sodium chloride. The solution of copper and rhodium salts was converted into a chloride solution and the pH adjusted to 1·3–1·5. Copper was selectively removed by the cation-exchanger Dowex 50W in the sodium form. Milligram amounts of rhodium were determined gravimetrically with thiobarbituric acid and microgram amounts spectrophotometrically with tin(II) chloride. The rhodium–copper filtrate was treated with the cation-exchanger to remove copper, and iridium was determined gravimetrically with 2-mercaptobenzothiazole or spectrophotometrically with tin(II) chloride. The method was applied successfully to the range of 5 mg to 50 μg of the two metals. Cross-contamination of the precipitates was negligible.

Formamidinesulphinic acid (thiourea dioxide) was used by Prokof'eva and Bukanova[52] to precipitate rhodium in the presence of iridium. The filtrate was treated to determine iridium gravimetrically, potentiometrically or polarographically. Following dissolution of the rhodium complex a tin(II) chloride spectrophotometric method was applied. The method was applied to amounts of 50–200 μg of rhodium and 50 μg to 23 mg of iridium in ratios from 1:10 to 1:100. The accuracy of recovery was about $\pm 4\%$ for rhodium and about $\pm 5\%$ for iridium: co-precipitation of iridium with rhodium increased with increasing iridium concentrations.

Multicomponent mixtures of the noble metals

A method of separating and and determining silver, ruthenium, rhodium and palladium, developed primarily for radiochemical separation, was recorded by Dehmlow and Preiss.[53] The procedure is classical in approach, with silver chloride precipitated first and purified by dissolution in ammonia. The combined filtrates were treated with sodium hydroxide and sodium hypochlorite and the ruthenium tetroxide was extracted with carbon tetrachloride and subsequently back-extracted into sodium hydroxide containing sodium hydrogen sulphite. Palladium was removed from the aqueous phase dimethylglyoxime and then rhodium by reduction with titanium(III) chloride. The authors considered the method suitable for semi-microquantitative applications, and 10–12 min sufficed to give reproducible quantitative separations of high chemical yield and high purity. The authors' conjoint use of the terms quantitative and high chemical yield is questionable and the data recorded do not support the claim for quantitative recovery, though recoveries should be quantitative if the time taken were extended.

Very few reagents provide a greater separational potential than sulphide salts or acids. On the other hand the resulting sulphide precipitates are seldom satisfactory weighing forms. Despite this fact, analytical recipes claiming success with the sulphides of noble metals continue to appear in current literature. Salaria[54] recorded procedures for the separation and determination of platinum in the presence of rhenium or zirconium and for gold in the presence of zirconium by a separational precipitation with sodium sulphide followed by adjustment of the hydrochloric acid concentration to 6*M* for platinum and to 1*M* for gold. In each case the noble metal sulphide was used as the weighing form. An error of 0·0–0·15% was claimed for 15–30 mg of platinum and 0·0–0·13% for 20–40 mg of gold. These methods were discussed in an earlier review.[55] It is emphasized again that the accuracy claimed requires verification by independent investigators.

Thermolysis curves for the sulphides of gold, platinum, ruthenium and palladium have been recorded by Taimni and Tandon.[56] Oven-dried gold sulphide gave a horizontal up to 220°, being converted into metal at 280°. In the case of platinum, Taimni and Salaria[57] had recorded previously that drying *in vacuo* at room temperature produced $PtS_2 \cdot 5H_2O$, and that at 130–135° the constant weight corresponded to $PtS_2 \cdot 2H_2O$. The later thermogram by Taimni and Salaria indicated that the air-dried pentahydrate lost water and sulphur from 50° to 310° at which temperature the metal was formed. The trihydrate behaved in exactly the same way. In the case of ruthenium the earlier work indicated the formula $Ru_2S_3.2H_2O$ for the product obtained by drying *in vacuo* to constant weight at room temperature. The later thermolysis curve indicated a loss of weight from 60° to 180° with a horizontal at 180–240° corresponding to an uncertain composition, then a gain in weight to 340° with a horizontal at 340–410°, again without a stated composition, then a loss of weight until the metal was obtained at 500°. In the case of palladium the earlier work[57] indicated a constant composition of $PdS.2H_2O$ after drying *in vacuo* at room temperature. The later thermogram[56] indicated a loss of weight by the air-dried precipitate from 50° to 420° with subsequent increases and decreases. From 800–840° the horizontal corresponded to PdO, the metal being formed at 890°. From the earlier work of Taimni and Salaria[57] the precipitate of $Ir_2S_3.10H_2O$ could be heated to 85° with the weight remaining constant. Although these authors did not record thermograms of this precipitate, Duval[58] recorded his failure to find any level of constant composition over the range 44–842°, which suggests that no iridium compound is formed that is suitable as a weighing form. The thermolysis curves provided

by Taimni and Tandon[56] do not provide evidence for the acceptability of the weighing forms recommended by Salaria and this failure does not encourage confidence in the sulphide methods described by Salaria.

A method of isolating platinum metals from partially refined concentrates was discussed by Zachariasen and Beamish.[59] The technique was designed to provide a method of dissolution of platinum metal concentrates which could be applied both to large scale operations and to analytical processes. Methods of isolation were included which would lend themselves to the precipitation of both large and small amounts of platinum metals. The concentrate used contained some 25 elements in addition to about 25% of platinum metals (including traces of osmium). Ths principal base metals included nickel, tin, copper, lead, chromium and iron, and silica was also present. Standard methods of dissolution, such as fusion with lead or zinc followed by treatment with acids, fusion with sodium peroxide, or chlorination with or without a sealed tube, were rejected for various practical reasons. The process finally accepted involved an intimate mixing of concentrate and sodium carbonate, sintering at 700° and leaching with water and acid. The dissolution resulted in a residue containng silica and a very small proportion of platinum metals, amounting to a total of about 2–3% of the original sample. The residue was readily fused with sodium peroxide. This sintering method resulted in very little corrosion of the container and could be made in a silica vessel. The sintered mass was coherent and could be taken from the vessel as a solid, dry body. In general, subsequent treatments involved classical separations which would lend themselves to large scale treatments. One distinct innovation involved a new method of separating rhodium from iridium, developed by Tertipis and discussed above. The results compared favourably with those obtained by spectrophotometric and spectrographic methods.

FIRE ASSAY

Although reports of solvent extraction separation of noble metals from aqueous media are numerous, relatively little has been recorded concerning the no less important solvent extraction by metals or alloys from fused media. Practically no data are available on distribution coefficients, stability constants of the dissolved constituents *etc.*, which would allow prediction of the effectiveness of extraction from the associated base metals, even for classical extractants such as lead. The phase diagrams for these alloys are of very limited assistance because the collecting alloy invariably requires a very high weight ratio of collector to noble metal. Furthermore, with the present very limited knowledge of the identity of the noble metal species in aqueous solutions of complex noble metal–base metal alloys, one must rely to a considerable degree on empirical approaches for the development of improved methods of separating noble metals from one another and particularly from high proportions of base metals. Very little progress in investigation of fire assay treatments has been recorded in English-speaking countries. On the other hand, such assay problems have received incomparably more attention in Russian laboratories. Recently, Shlenskaya[60] reviewed some of the Russian developments in noble metal analysis and stated that "conferences on the analysis of noble metals, in which workers from research institutes and plant laboratories participate, are regularly held in the Soviet Union." The present author has made a considerable effort to secure copies of the original Russian publications which deal with the separation and determination of the noble metals but with little overall success. Wherever possible, however, pertinent material in the various abstracts has been included.

An excellent general discussion of the problems associated with each stage of the fire assay processes was recorded by Britten.[61] His comment on the future status of fire assay is of some interest; "In common with gold assaying elsewhere the classical methods of fire assay have continued to withstand all competition from the new methods of chemical analysis which have been adopted as standard practice in other fields." He outlined the steps which are being taken to reduce the various errors caused by pulverizing, cupellation, parting *etc.* It was considered that for existing processes of cupellation "The absorbed gold under good conditions of assay varies from about 0·5 to over 2% being inversely proportional to the weight of the final bead" and under specific conditions the oven assay is reasonably in balance with the measured losses of gold in the cupellation stages. The author concluded that a rise in the price of gold would encourage researches designed to produce increased accuracy of determination.

In an interesting paper, Hanrahan[62] stated that the results from two streams of assaying showed that the maximum differences in results were 2 parts per 10000. In discussion of the optimum gold–silver ratio for cupellation he stated that the absorption of gold by the cupel tended to decrease with increasing proportions of silver. The ratio of silver to gold of 2·5 represented the highest concentration of silver which could safely be subjected to normal acid parting.

Among the reports which deal with the losses of gold during the various stages of a fire assay, Coxon, Verwey and Lock[63] have shown that routine mine assays give values about 2% too low, the losses being made up as follows; 0·5% of gold to crucibles, slags, and button dressing, 0·7% to cupel, 1·2% dilution by iron during pulverizing. These losses are partially compensated for by the 0·4%

of silver retained from the bead after parting. Sinclair[64] pointed out that for samples which require little or no pulverizing the 1·2% loss can be neglected and for those cases where the silver retention by the gold is higher there may be a compensation of errors. Sinclair also reported on the amount of gold lost to slags and cupels and compared these losses with the silver content retained after parting. To determine the slag losses he made 132 residue fusions, the slags from which were remelted and re-assayed without crushing: the loss to slags was 2·20%. Losses to the slags and cupels, determined from 44 residue fusions without crushing, were 2·59 and 0·52% respectively. In the latter case, drillings with ¼-in. drill to a depth of ⅜ in. were used. The actual loss was reduced by 1·91% because of silver retention in the parting acid. The gold content of the litharge averaged 0·0036 mg for 4·3 g. Experiments with crushed slags and cupels which showed a nett loss of 12·82% indicated an appreciable contamination from the manganese-steel jaw-plates, and a direct determination on 8·12 g of skimmings from the latter yielded 0·041 g of gold. The nett loss on large composite samples of residues averaged 1·27% the slags from the fusions were not crushed. In a similar experiment in which the slags were crushed the apparent nett loss of gold was 9·35%. Salted composite samples, for crucibles washed with litharge, yielded results 2·23% low and for unwashed crucibles 1·36%: salted barren silicate samples yielded corresponding values low by 2·24% and 1·25%.

For the determination of gold in ores, concentrates and cyanide eluates, Linhart[65] rejected the polarographic determination because of losses of up to 50% caused by adsorption on voluminous precipitates such as silver chloride and iron hydroxide. He calcined the samples and formed a lead–gold button by fusion at 800–900° in the presence of borax and sodium chloride The lead was cupelled to form a silver bead which was parted in nitric acid. The parting acid was drawn off by suction and the gold dissolved and determined polarographically. To determine gold in biological material the latter was ignited and treated as described above.

For the determination of gold in ores, Bagdasaryn[66] used a wet extraction of 50–100 g with nitric acid, leaching 7–8 times. The dried residue was treated with *aqua regia*; the mixture was evaporated and treated with hydrochloric acid. The chloride filtrate was evaporated to small volume and neutralized to litmus. Gold was precipitated by excess of standardized iron(II) sulphate, the excess being back-titrated with potassium dichromate with *N*-phenylanthranilic acid as indicator.

Aluminium–gold alloys cannot be cupelled directly because of the oxidation to aluminium oxide. Scherfaufer[67] selectively dissolved the aluminium with 5*M* sodium hydroxide and filtered the gold. The paper was ashed in lead foil which was then fused to produce a lead button. Gold was then determined conventionally by cupellation.

An assay method for the determination of gold in materials containing high proportions of iron or chromium was recorded by Maslenitskii *et al.*[68] Iron oxide was removed by dissolution in hydrochloric acid and chromium oxide by *aqua regia*. Gold was then determined by precipitation and cupellation.

One of the most exhaustive examinations of the fire assay process for the collection of nanogram amounts of the noble metals was described by Beyermann.[69] The fusion technique was varied somewhat in that a little flour and lead granules were added subsequent to the fusion at 900°. The fusion mixture contained litharge, borax, silica, sodium carbonate and flour. Re-fusions of the slag were also made and the lead buttons were then combined. Standard cupels as well as some prepared from bonemeal and Portland cement were used for cupellation after preheating at 900°. In general, the noble metal content was about 1 ppm. The samples analysed were galena, feldspar, roasted ore and a synthetic galena. The author's results agreed with previous findings that collection by silver beads was ineffective for nanogram amounts of iridium, ruthenium and rhodium but relatively complete for gold, palladium and platinum.

Losses of radioactive palladium, platinum and gold during the parting process with either concentrated sulphuric acid or 50% v/v nitric acid were investigated. The parted residue was filtered through media with 1-μ pores and the radioactivity of the filtrate was measured. For 10-mg beads and platinum contents ranging from 0·02 to 1·8% the relative losses after parting with nitric acid ranged from 19 to 2% respectively for these extremes. In the case of sulphuric acid the relative losses were 0·04% for 0·1% of platinum and 6% for 0·003% of platinum. For 0·01% of rhodium, with sulphuric acid the relative loss was 81%, slightly reduced when small amounts of platinum were associated with the rhodium. Parting gold–silver beads with sulphuric acid resulted in a relative loss of 0·4% for 1·0% of gold and for 0·005% a loss of 0·8%.

Investigations were made of losses to the container wall during evaporation of aqueous solutions of rhodium, ruthenium and gold and subsequent heating of the residues to 120° and 400°. Solutions of 50 and of 2 ng of rhodium, gold and ruthenium were evaporated in such a way that the residue covered an area of 1–2 cm^2. Following evaporation the residue was heated for 10 min. After cooling the area was rinsed twice with 1*M* hydrochloric acid and the activity was then measured. With the residue heated at 120°, the losses of rhodium, ruthenium and gold to glass were respectively 0·8, 0·7 and 9·5%. At 300° the losses were appreciably higher. With quartz, the corresponding losses were

appreciably smaller. The activities retained in the container were not significantly removed by treatment with hydrochloric acid: chlorine and bromine were without effect, but short treatments with hydrofluoric acid eliminated the activities.

The effects of associated metal constituents on the efficiency of various extractions of each noble metal were examined. The noble metal was present in concentrated hydrochloric acid or ammonia solution. In each case 2-ng, 50-ng and 2-mg amounts of noble metal were used along with the associated metals, including silver and lead. The extractants for which there was no appreciable influence from associated metals were tributyl phosphate in benzene (10 mg of associated metal): n-octylamine and tri-n-octylamine in chloroform (50 mg of associated metal): butylamine in chloroform (from ammoniacal media): the extraction of 50 ng of rhodium, ruthenium and iridium with sodium diethyldithiocarbamate in chloroform from sodium carbonate or ammonical media was not affected by 10 mg of platinum, palladium or gold: 2 μg of rhodium could be extracted in the presence of uranium or thorium. Special precautions were necessary for the separation of rhodium, iridium and ruthenium from ammoniacal solutions of platinum, palladium and gold. Extraction of 10 ng of gold from hydrobromic acid was 99·8% complete: furthermore, in the presence of 50 mg of platinum, palladium rhodium and iridium and 50 mg of gold, only traces of the platinum metals were co-extracted. With dimethylglyoxime in ethanol and chloroform 50 ng to 1 mg of palladium could be extracted from solutions containing platinum, rhodium, iridium, calcium or aluminium chloride: only 1–2% of the noble metals were found in the chloroform layer.

The efficiency of co-precipitation of 2 and 50 mg of noble metals with the common precipitants and collectors was investigated. These were lead and rhenium sulphides, mercury mixed with mercury(I) chloride, selenium silver and lead chlorides, and various hydrous oxides. In the case of lead sulphide, additions of 10 g of nickel, aluminium, calcium and sodium were without adverse influence. Co-precipitations of the sulphides of rhodium, iridium and ruthenium with rhenium sulphide required the application of pressure. With selenium, co-precipitation was accomplished by sodium sulphite in sulphuric acid medium. In the presence of 50 mg of silver and 2 ng of the noble metals 24% of the silver was co-precipitated, and if 0·1 mg of silver was present, 80% of it was co-precipitated. Co-precipitation of the platinum metals with a mixture of mercury and mercury(I) chloride was unaffected by high proportions of iron, nickel and gold. Co-precipitation of palladium with silver chloride has been a consistent problem in the parting of noble metal–silver assay beads. Beyermann found that dissolution of the silver chloride in ammonia and reprecipitation of the silver chloride removed two-thirds of the co-precipitated palladium: the results for a solution containing 2 μg of the noble metal and 10 mg of silver are of some significance—the amounts of iridium(IV) palladium(II), gold(III), platinum(IV) and rhodium(III) co-precipitated were 95, 19, 9, 3 and 2% respectively. In the case of 1 g of lead as the chloride in the presence of 2 and 50 ng of rhodium, 2 and 4% respectively of the latter were co-precipitated.

He also dealt with co-precipitation of the noble metals with iron hydroxide from various aqueous media. From 2*M* ammonia solution containing 50 ng of rhodium(III), gold(III), platinum(IV), iridium(IV) and palladium(II) the recoveries were 59, 35, 45, 24 and 3% respectively. Results were given for solutions of sodium acetate and concentrated ammonia. In the case of the potassium bromate hydrolytic method of Gilchrist and Wichers[70] it is noted that in the presence of 5 mg of nickel, iron, palladium or rhodium the amount of platinum(IV) co-precipitated from a total of 50 ng was 2, 4, 4 and 5 ng respectively. Similarly, small amounts of gold were also co-precipitated, particularly in the case of 50 ng of palladium. About 2 ng of platinum(IV) were co-precipitated in solutions containing 25 mg of rhodium, palladium or iridium and 50 ng of platinum(IV).

The author's investigation of the separation by ion-exchange resulted in some unexpected conclusions. Dowex 1 was used to adsorb gold, platinum and palladium in 6*M* hydrochloric acid. Only 5–15% of the anions could be eluted with concentrated hydrochloric acid. Continued treatment removed two-thirds of the metals, and eluting media such as 2*M* ammonia were less effective. Recovery was accomplished sucking the resin dry, mixing it with litharge and fusing. Treatment of the lead regulus resulted in complete recovery of either 10 μg or 50 ng of rhodium. In the case of 50 ng of rhodium along with 50 mg of palladium, iridium or platinum, the recoveries of rhodium were 92, 100 and 97% respectively, the other three metals remaining adsorbed. In the present author's opinion, these results require some confirmation.

The author's results dealing with losses by evaporation were significant. Solutions containing 5 ng to 2 mg of ruthenium could be fumed with hydrochloric or nitric acid or *aqua regia* without loss, but in the presence of 25 mg of osmium and 10 ng of ruthenium 1% of the latter was lost on fuming with concentrated nitric acid. For the volatilization of 10 ng to 5 mg of ruthenium the author preferred sulphuric acid–bromate, hypochlorite (chlorine in alkaline solution), and perchloric acid to the sulphuric acid–dichromate oxidation. In contrast to other oxidizing media, perchloric acid avoided the introduction of oxidizing media into the receiving solutions and thus losses of ruthenium. Nitric acid was an effective oxidant for osmium but the receiving liquid of hydrochloric acid required

saturation with sulphur dioxide, and losses of osmium resulted from boiling off the hydrochloric acid.

Beyermann proposed three methods of treating silver beads. One applied to beads containing no more than 10 μg of gold or platinum. A second was intended for the determination of gold and palladium only. These two procedures involved combinations of standard treatments such as parting with sulphuric acid. Techniques were included for the recovery of palladium adsorbed by the silver chloride and for the isolation of palladium by extraction of the dimethylglyoximate by chloroform. Palladium was finally determined amperometrically. The "insoluble" residue of gold or platinum from the parting treatment was treated with *aqua regia* and fumed with perchloric acid, and gold was extracted as the bromide by diethyl ether and finally determined amperometrically. Platinum in the aqueous phase was also determined amperometrically.

The third method involved parting the bead with sulphuric acid, then adding selenium dioxide and sodium sulphite to the mixture. The residue, of gold, platinum, palladium and part of the silver, was dissolved in *aqua regia* and fumed to remove the selenium. Gold as the bromide was extracted by ether, followed by extraction of palladium dimethylglyoximate from the aqueous phase by ether, and then platinum was determined as in the first two methods. The results recorded for salted solutions indicated good recoveries of gold, palladium and platinum in microgram and submicrogram amounts. In each case, the solutions contained a second noble metal from which there was no significant interference. The methods were also applied to a variety of noble metal products such as roasted ore, iron ore, slags, silver coins and lead, generally with an accuracy acceptable in comparison with other methods. For the iron ore the values obtained by a spectrochemical method for gold, platinum and palladium were 0·09, 0·24 and 0·4 respectively as compared with the author's values of 0·13, 0·10, 0·21.

The present author's efforts to secure copies of original Russian publications dealing with the fire assay for noble metals met with little success. Consequently, most of the information included below has been obtained from various abstracts and thus details of significance may be lacking.

In order to ensure thorough mixing of the pot charge during the assay procedure for noble metals Anisimov *et al.*[71] arranged for mechanical mixing during the smelting process: the initial heating procedure was slow and super-heating was applied at the conclusion of the fusion. An excess of reducing reagent was required with a limited amount of litharge, part of which was added as a solution of lead acetate in order to secure uniform distribution and intimate contact with the noble metals. One may assume that the moistening process involves wetting the whole of the pot charge. Light and fluid slags were obtained with the ores used and the acidity of the charge varied between 1 and 1·5. The authors noted that impurities collected by the lead button assisted in the extraction of the platinum metals. In the case of noble metal concentrates, the accuracy of recovery was increased by resmelting the slag and the cupel.

Anisimov and his co-authors made several reports dealing with the fire assay of the noble metals. The losses of platinum metals at each stage of the assay of concentrates was studied.[72] The techniques included the preparation of a silver–lead button, scorification, reassay of slags and cupels, and the analysis of the silver bead. The ratio of noble metals to silver in the bead was 1:15 or 1:20, but in the case of high iridium was made 1:40. The fusion was carried out at 1000–1050° for 1·5 hr. The 40-g lead buttons were scorified to 18·25 g. The cupellation temperature was 900–950°. The authors included the losses to slags and cupels for platinum, palladium, rhodium, iridium and ruthenium. The amounts recovered from two silver beads were respectively 100·0 and 100·0, 99·9 and 100·0, 99·5 and 99·7, 98·3 and 100·0, 99·2 and 99·9%. Small amounts of selenium or tellurium were without effect. A separate lead button was used for ruthenium. The authors found that reassay of the first pot slag, and of the cupel, was required for good accuracy. To combine two silver beads, fusion was made in a chamotte crucible under a layer of soda, borax, and wood charcoal. Anisimov *et al.*[73] also provided a detailed description of a method for treating silver assay beads. These were parted with nitric acid and the residues were treated with *aqua regia* to dissolve the gold and platinum. The former was finally precipitated with sulphur dioxide and the latter as ammonium chloroplatinate. The residue from the *aqua regia* treatment was sintered with barium oxide, the sinter was treated with hydrochloric and sulphuric acids and the barium sulphate was removed. The filtrate was evaporated to fumes and sodium bromate was added to produce ruthenium tetroxide which was distilled and determined by potentiometric titration. The pot-liquid was boiled with hydrochloric acid to destroy the bromate, and sodium nitrate free from ammonium or potassium ion was added. Sodium sulphide was added to precipitate the rhodium and any residual platinum. The precipitate was dissolved in *aqua regia*, and later evaporated with hydrochloric acid. Platinum was again precipitated as ammonium chloroplatinate. The filtrate was treated with zinc to precipitate the rhodium, which was purified by fusion with silver under borax to remove contaminants. Iridium in the filtrate from the sulphide precipitation was finally determined potentiometrically.

For the determination of gold and silver in ores, Anisimov *et al.*[74] prepared a second lead button from the scorification and crucible slags and scorified the two buttons. Gold was determined by a potentiometric titration with hydroquinone.

The techniques and principles involved in fire assay methods were reviewed by Anisimov.[75] The function cupellation and scorification was outlined and methods for determining osmium and ruthenium were discussed. In particular, the author included a description of the wet methods of parting and determining the constituents in a noble metal–silver bead.

Methods of preparing ore concentrates for the assay of platinum metals were discussed by Anisimov *et al.*[76] The concentrates included copper–nickel ores, mattes, cementates, and other products containing large amounts of selenium, tellurium, arsenic, and antimony. The finely ground product was mixed with sawdust, sulphur and concentrated sulphuric acid, and was heated first at 240–300° and then at 375° for 2 hr. The powdered sinter was mixed with aqueous starch, dried, and again heated at 375° for 1–2 hr. The sinter was leached with water and the residue was fused. If appreciable selenium, tellurium, arsenic, tin and antimony were present the sample was chlorinated after mixing with sodium chloride and charcoal and wetting with starch to form granules: these were dried in a desiccator and heated in a tubular oven for 4 hr at 500–550° in a chlorine current. A single treatment removed up to 95% of the selenium and tellurium. If the sample contained iridium or ruthenium as well as copper the residue was subjected to two sulphuric acid treatments. The presence of copper in the lead assay button encouraged dissolution of ruthenium and iridium by the nitric acid parting solution.

Anisimov *et al.*[77] found that a spectral analysis of assay beads obtained from low-grade products increased the overall sensitivity of determinations relative to classical methods and thus permitted the use of smaller weights of samples than those normally used for fire assay: 50-mg silver–rhodium and copper–ruthenium–iridium beads were used. These were obtained from the residue of the lead parted with dilute nitric acid. The authors stated that when the weight ratio of platinum and palladium to ruthenium and iridium was less than 100, the latter two metals could be determined spectrochemically, without a separation of platinum and palladium. When the weight ratio was 200, the residue from the silver bead could be treated with *aqua regia*. It is most unfortunate that the details of the spectrochemical methods were not available. Normally, one of the most important problems is the necessity of achieving homogeneity in the beads or residues used by these authors. They stressed again the influence of copper and nickel which caused some dissolution of iridium and ruthenium in the button parting acid. A scheme of analysis of ores and their concentrates for rhodium, ruthenium and iridium was included.

For almost a century following the discovery of the platinum metals the only effective general method for the determination of these metals in ores involved a collection by molten lead from fused media of suitable composition. Furthermore, there can be little doubt that this method suggested itself through the similarity in properties of the platinum metals and gold, for which the assay-metallurgical method had been an ancient procedure. It is only within the past few years that organized investigations have been made to determine the effectiveness of lead as a collector for each of the six platinum metals and indeed even for gold. The results of these investigations, made in various parts of the world, are in approximate agreement that for such metals as gold, platinum, palladium, ruthenium, osmium and perhaps for rhodium the lead collection is effective for amounts of the order of small fractions of a milligram. Thus the classical fire assay will reveal commerically valuable noble metal values for all ores and concentrates although quantitative success will depend upon the assayer's experience and wisdom in the choice of technical conditions. Much of the early work which was concerned with the examination of the efficiency of classical fire assay has been reviewed.[78] Results were obtained which indicated some lack of efficiency of the fire assay for iridium. Because of this and the desirability of having available alternative assay methods for noble metals, various researchers developed procedures which involved collectors other than lead.

Tin has been used as one alternative. In a series of papers Faye and co-workers[79–87] have developed a scheme of separation of noble metals incorporating spectrophotometric methods of determination. The various steps in the method were each carefully proved and the method as a whole was applied with success to copper–nickel matte, precious metal concentrates, meteorites, and iridosmine. Although Faye provided a procedure for the continuous determination of the seven noble metals from a single sample, variations in procedure allowed for simplified determinations of certain noble metals in the absence of others. If the ore contains much sulphur or arsenic it is roasted at 750–800° to avoid the formation of a matte or speiss. For samples containing high proportions of copper and nickel a leaching process is recommended. In general, the precious metals are collected in molten tin when the sample is fused at 1200–1250° with a flux containing tin(IV) oxide, sodium carbonate, silica, borax and powdered coke. The resulting tin alloy is placed in a graphite crucible and melted at 600–700° in an atmosphere of nitrogen and then poured into a gallon of water to disintegrate the button. The liquid is decanted and the particles of noble metal–tin alloy are dried. These are parted in concentrated hydrochloric acid and if osmium is present the tetroxide is distilled in the presence of hydrogen peroxide, collected in hydrobromic acid[79] and determined with pyrogallol.[80] The pot residue is treated with hydrochloric and hydrobromic acids to volatilize the tin. In the absence of

osmium this treatment is applied directly to the solution of the noble metal residue produced by adding tin to the hydrochloric parting acid.

The mixed halide solution is treated to remove gold by extraction with diethyl ether and determined with *o*-tolidene.[81] At this stage, if more than 2 g of base metals are present they are removed by cation-exchange, and then the acid solution of the remaining noble metals is treated with perchloric acid to volatilize the ruthenium tetroxide which is collected in concentrated hydrobromic acid and determined spectrophotometrically.[79] The perchloric acid in the pot solution is removed by evaporation with hydrochloric acid* and with *aqua regia*, and further evaporations with hydrochloric acid. The chloride solution is treated with sodium iodide, and rhodium and iridium are extracted with tri-n-butyl phosphate (TBP) in hexane.[82–85] These metals may be separated by a modification of the method of Yoe and Kirkland,[88] in which case the palladium *p*-nitrosodimethylaniline complex is extracted from the aqueous phase by chloroform. The aqueous phase is treated with sulphuric and perchloric acids and platinum is determined with tin(II) chloride. The TBP–hexane phase is evaporated nearly to dryness and nitric acid is added to destroy the iodides. The metal salts are then converted into chlorides and hydrogen peroxide is added to ensure oxidation to iridium(IV) which is extracted by TBP–hexane, stripped by hydrochloric acid and finally determined with tin(II) chloride in hydrobromic acid. Rhodium in the aqueous phase is reconverted into the chloride complex and the solution is evaporated to dryness. The metal is determined with tin(II) bromide in perchloric acid.

The complete procedure, including a number of variations, depending upon the number of metals present and their proportions, was recorded by Faye.[86,87] The reports bear the marks of carefully applied techniques and the results are excellent.

Recent researches, reviewed earlier by the present author,[78] have indicated that the composition of the flux used for the classical assay may affect the recovery of iridium, basic slags producing relatively high losses. High losses also occur in the presence of much copper and nickel. To explain these losses it was suggested that the lead collector, which has a minimum crystal size factor of 3·00 Å, is above the theoretical size required for a good solvent of precious metals. Thus, the collection of iridium by lead is probably achieved largely through mechanical processes. This and other deficiencies in the quantitative collection of iridium by classical fire assay led to the investigation of other approaches. Because of the regular occurrence of copper, nickel and iron with the platinum metals it seemed probably that these metals could serve as collectors in a fire assay. One would guess too that the disintegration of the base metal silicates and the noble metal constituents would occur simultaneously and that their juxtaposition would thus encourage the efficiency of collection. The base metal buttons were prepared by reduction with mechanically mixed graphite, soda ash, borax, and ore with base metals added if required. The buttons were placed in standard distilling equipment together with hydrochloric acid (3 + 1) and a stream of nitrogen was passed through.[89] Heat was applied to accomplish dissolution Any small amount of osmium tetroxide developed during this treatment was collected in a receiver trap containing hydrochloric acid into which sulphur dioxide was bubbled. The content of the distillation flask was heated to yield a moist chloride cake which was moistened with water and allowed to stand overnight exposed to the atomsphere. The mixture was then diluted with water and filtered. The filter paper and residue were treated in the distillation flask with sodium hydroxide solution, chlorine was passed through and any osmium and ruthenium tetroxide were collected in hydrogen peroxide. This solution was added to the pot-liquid as indicated below. The filtrate from the pot-liquid was diluted with water, the pH adjusted to 0·9–1·5 and the base metals selectively removed by a cation-exchanger which was then washed with hydrochloric acid at pH 1 (see also reference 90). The effluent was treated with a stream of sulphur dioxide for 1 hr followed by a 6-hr standing period. The solution was evaporated to 500 ml on a hot-plate and subsequently to 15 ml in the distillation flask under an atmosphere of sulphur dioxide.

This solution was combined with the osmium and ruthenium from the filter paper and residue as indicated above, and then treated as described by Westland and Beamish[91] to remove osmium, and the pot-liquid containing the remaining platinum metals was also treated by Westland's procedure to remove ruthenium.

The pot-liquid now contained all of the platinum, palladium, iridium and rhodium. Rhodium and iridium may be separated and determined as described by Tertipis and Beamish[51,92] or by Sant and Beamish[93] and also by the various other methods recorded above. Platinum and palladium may be separated and determined as described by Coburn *et al.*[94] and by Plummer.[95]

The physical characteristics of the iron–copper–nickel–noble metal alloys were described by Plummer *et al.*[95] It was concluded that palladium and probably some of the other platinum metals form solid solutions with the alloy.

* Recent researches by the author have shown that though perchloric acid is removed by evaporations with hydrochloric acid and/or treatment with *aqua regia*, the removal is not sufficiently complete to allow the subsequent use of a cation-exchanger for the separation of decagram amounts of base metals.

The iron–copper–nickel collection was applied to determine the composition of iridosmines. Sen Gupta and Beamish[97] found that the fusion allowed the dissolution of even such resistant alloys as Tasmanian iridosmines. The results obtained by the method agreed with those from a chlorination of the iridosmines.

The iron–copper–nickel collection was used by Kavanagh and Beamish[98] to collect osmium and ruthenium quantitatively from roasted sulphide ores. The method involved parting of the alloy and distillation of the tetroxides of osmium and ruthenium from perchloric acid. Thiourea in 6*M* hydrochloric acid was used as the collecting liquid when both metals were distilled simultaneously, and hydrobromic acid when ruthenium only was distilled. The metals were precipitated as the thionalide complexes. Perchloric acid was also used for the dissolution of siderite meteorites.[99] The platinum metals were separated and determined as in the case of the iron–copper–nickel assay button.

This fire assay for osmium was extended to apply to sulphide concentrates. This adaption avoided the oxidation previously used by Kavanagh to eliminate sulphur, a process which could cause the loss of osmium. Van Loon and Beamish[100] used hydrogen to reduce the sulphur content to a level which allowed a clear fusion. For flotation concentrates, salted with 16–805 μg of osmium per assay ton, only microgram losses were found.

Because of the high temperature required for the fusion of iron–nickel–copper buttons an effort was made to reduce the required temperature by the addition of copper to the ore. Banbury and Beamish[101] collected platinum and palladium quantitatively in this way. Buttons of 25–40 g in weight were prepared from a roasted artificial sulphide containing 81·5 g of copper sulphide. The palladium content varied from 40 μg to 10 mg: the platinum content from 50 μg to 10 mg. Recoveries were acceptable in all cases. Initial furnace temperatures were 1100° and were raised to 1200° over a period of 1·5 hr. The chemical treatment involved the removal of copper by cation-exchange from the parting solution adjusted to pH 1·0 $\pm$ 0·1. By a similar process, Banbury[102] collected rhodium by means of copper. As in the case of platinum and palladium, losses to siliceous residue, slag, pot-wall, and ion-exchange resin were found to be negligible. Copper was also used as a collector or iridium. Agrawal and Beamish[103] considered copper superior to lead for the collection of iridium in that it can be applied successfully in the presence of the commonly associated transition metals. It was superior to copper–iron–nickel in that comparable collections could be made at lower temperatures. Maximum recovery was achieved with acid slags of 3·0 silicate degree.

Despite the availability of new collectors for the noble metals, the classical lead collector remains clearly superior for the determination of platinum, palladium, gold and perhaps rhodium. The device of cupellation to remove the lead selectively requires very little attention and it is a reasonably rapid process compared to the methods required for the removal of copper, nickel, iron or tin. Furthermore, the ease of forming a silver–noble metal alloy by cupellation allows use of a variety of potentially useful methods of separation and determination. It should be noted that though osmium is collected quantitatively by lead, cupellation is not acceptable because of losses of osmium tetroxide, and any attempt to form a silver bead will increase the osmium losses. On the other hand, the removal of both osmium and ruthenium from lead by a parting distillation with perchloric acid is accomplished with ease.

For those analytical consultants who frequently must deal with the claim that the classical lead collection will sometimes fail to reveal noble metal values of commercial importance, the present author emphasizes the fact that no valid support has ever been recorded for this claim and one cannot doubt that the classical method used by competent assayers will invariably indicate whether a noble metal content is of commercial value.

Zusammenfassung—Diese Übersicht handelt von den Trennungen der sieben Edelmetalle durch Chromatographie, Fällung oder Schmelzverfahren, die zwischen den früheren Übersichten und Januar 1966 publiziert wurden. Die in Lösung vorliegenden Edelmetallspezies werden diskutiert, sofern sie zur Trennung und Bestimmung in Beziehung stehen.

Résumé—Cette revue traite des méthodes de séparation des sept métaux nobles par chromatographie, précipitation et voie sèche, publiées ultérieurement aux précédentes revues et antérieurement à janvier 1966. On discute des espèces chimiques sous lesquelles les métaux nobles sont présents en solution dans la mesure où elles sont reliées à la séparation et au dosage.

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STUDIES IN ATOMIC-FLUORESCENCE SPECTROSCOPY—V*

THE FLUORESCENCE CHARACTERISTICS AND DETERMINATION OF ANTIMONY

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Summary—Atomic-fluorescence of antimony may be generated in an air-propane flame by nebulizing aqueous solutions of antimony salts whilst irradiating the flame by means of a microwave-excited electrodeless discharge tube operating at 30 W. The strongest fluorescence is exhibited by the $^4S_{1\frac{1}{2}} \rightarrow {}^4P_{\frac{1}{2}}$ 2311 Å resonance line and weaker signals are observed at the 2068 and 2176 Å resonance lines and at four intercombination lines, at 2598, 2671, 2770 and 2878 Å. A process of thermally assisted direct-line fluorescence is postulated to account for the otherwise inexplicable intensity of the 2598 Å line emission. Atomic-fluorescence spectroscopy at 2176 Å permits the determination of antimony in the range 0·1–120 ppm with a detection limit of 0·05 ppm. With the same equipment and source, the range of measurement for atomic-absorption was 6–120 ppm and the detection limit was 1 ppm. No interferences were observed from 100-fold molar amounts of Cd, Co, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, NH_4, Pb and Zn or from arsenate, chloride, nitrate, phosphate and sulphate.

THE determination of antimony by flame emission methods presents numerous problems. The ground state atoms of antimony are difficult to excite by thermal means and the only emission studies to date[1,2] have been carried out by using the inner cone of an oxy-acetylene flame in conjunction with nebulized organic solvents. The principal resonance lines at 2068, 2176 and 2311 Å lie in the far ultraviolet and give rise to low sensitivities because of the poor response of most photomultipliers in this region. In addition, antimony hollow-cathode lamps give a low radiation output at the resonance wavelengths. In spite of this, successful atomic-absorption measurements have been made by Gatehouse and Willis, using a hollow-cathode lamp at 3211 Å.[3] The 2176 Å resonance line gave the strongest absorption, but there was less noise at the 2311 Å resonance line because of its higher intensity as detected by the photomultiplier. The limit of detection was given as 1·5 ppm. Atomic-absorption studies have also been made with a continuous source[4] and photographic recording of line intensities. The limit of detection of this method was estimated to be 0·5 ppm.

The following communication reports some of our more recent observations with antimony in the development of atomic-fluorescence spectroscopy as an analytical technique.

* Part IV—*Talanta*, 1967, **14**, 557.

EXPERIMENTAL

Apparatus

The apparatus for exciting the discharge tube and recording the fluorescence has been described previously.[5,6]

Preparation of discharge tube. Quartz tubes 3–4 cm long and 0·8 cm in internal diameter, prepared as previously described,[6] were heated to redness with an oxy-propane blow-torch and subjected to evacuation for about 10 min, during which argon was periodically flushed through the system to sweep away any impurities liberated from the walls of the tubes. The tubes were cooled under vacuum and then removed from the vacuum line, and about 10 mg of electrolytic antimony were added to each. The tubes were then evacuated, heated so that the antimony just melted, and flushed three times with argon to remove any occluded gases or volatile impurities in the antimony. After cooling, 10 mg of iodine were introduced and the tubes were evacuated and periodically flushed with argon for about 5 min to remove any moisture liberated from the added iodine (heat cannot be used because of the volatility of iodine). The tubes were finally sealed under an argon pressure of 0·5–5 mm Hg. An excess of antimony over that required for the formation of antimony(III) iodide was maintained to eliminate free iodine, the intense spectrum of which would otherwise have been emitted.

Reagents

Antimony solution, $10^{-3}M$. Dissolve 0·3249 g of potassium antimony tartrate in distilled water and dilute to 1 litre; 1 ml ≡ 121·8 μg of Sb.

Atomic-fluorescence measurements

Flame conditions. A non-luminous, fuel-rich, air–propane flame was obtained with a propane jet in the standard burner base together with the circular propane emission burner-head, the air pressure being 15 psi and the propane pressure 12 cm on the di-n-butyl phthalate filled manometer. The top of the burner-head was set 3 cm below the centre of the monochromator slit. The SP900A is used in its "emission" mode for atomic-fluorescence measurements.

Source conditions. An antimony microwave discharge tube was operated at 30 W with the end-cap off the cavity and with a moderate degree of cooling applied by blowing compressed air through the cooling aperture. The source was placed *ca.* 8 cm from the centre of the burner-head, at right-angles to the line between the flame and the monochromator slit. A 5-mm slit was cut in the burner-housing to allow irradiation of the flame.

Procedure for 1·2–12 ppm of Sb. Transfer by pipette 1–10 ml portions of $10^{-3}M$ antimony solution into a series of 100-ml volumetric flasks and dilute to volume with distilled water. Nebulize the solutions into the air–propane flame and, using a slitwidth of 0·3 mm, a gain of 3,1, and bandwidth 3, measure the fluorescence signal at 2176 Å.

Other concentration ranges, *i.e.*, 10^{-4}–$10^{-3}M$ and 10^{-6}–$10^{-5}M$, may be measured by suitable dilution of the stock solution and adjustment of the slitwidth and gain controls.

Atomic-absorption measurements

Flame conditions. A non-luminous fuel-rich air–acetylene flame was obtained with an acetylene jet in the burner base and the 7-cm long acetylene burner-head, the air pressure being 15 psi and the acetylene pressure 9 cm on the di-n-butyl phthalate filled manometer. The top of the burner head was set 1 mm above the bottom of the monochromator slit.

Source conditions. An antimony microwave discharge tube was operated at 20 W with the end-cap off the cavity and with only slight cooling applied as described above. The source was placed in the usual position for atomic-absorption measurements on the SP900A, but slightly out of focus to prevent too much light reaching the photomultiplier. The SP900A was used in its "absorption" mode.

Procedure for 6–122 ppm of Sb. Transfer by pipette 2·5–50 ml portions of $10^{-3}M$ antimony solution into a series of 50 ml volumetric flasks and dilute to volume with distilled water. Nebulize into the air–acetylene flame and, using a slitwidth of *ca.* 0·01 mm, gain 2,3 and bandwidth 3, measure the absorption at 2176 Å.

RESULTS AND DISCUSSION

Characteristics of discharge tube.

The ground state of the antimony atom[7] is $^4S_{1\frac{1}{2}}$ and a simplified Grotrian diagram is shown in Fig. 1. All the lines shown in this diagram were observed as well as higher state lines which are accounted for by Brode.[8] In addition, the 2062 Å iodine line was very prominent, but the continuum associated with tubes containing free iodine was absent.

The tube was run at 30 W and the resonant cavity was air-cooled by forced draught. Tuning was very critical and there were two modes of tuning. The first was obtained by screwing the larger of the two coupling probes fully into the cavity; the discharge obtained rapidly reverted to an argon discharge. The other was obtained by unscrewing the large probe about three complete turns. This gave an intense stable output. The variation in response was $\pm 1\%$ over a period of 1 hr.

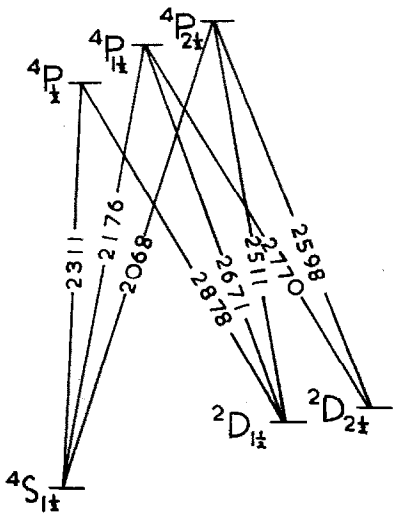

FIG. 1.—Simplified Grotrian diagram for antimony.

Close to the 2176 Å resonance line there is a non-resonance line at 2179 Å which, according to Brode,[8] is slightly more intense in the spark than in the arc spectrum. The 2176 Å resonance line however, is, only an eighth as intense in the spark as in the arc spectrum. Both lines are equal in intensity in the spark spectrum and the photomultiplier response over such a small range in this region can be considered to be constant. Hence, from the relative intensities of these two lines at various operating power ratings and rates of cooling, the exact type of discharge can be evaluated.

It was found that with the microwave-excited source the ratio of the line intensities (2176:2179 Å) decreased with increasing power ratings. At 15 W the ratio was *ca.* 3, whilst at 50 W the ratio was *ca.* 0.7. The ratio increased rapidly with increased cooling, but the absolute line intensities decreased. At relatively high power ratings ($>$ 30 W), the change of intensity (I) with power (p) (*i.e.*, dI/dp) fell to *ca.* 0·3 for the resonance line, but was approximately unity for the non-resonance line. It would appear from this that at these higher operating powers self-reversal (and possibly self-absorption) occurs. The optimum power for operation was considered to be about 30 W for a tube containing an argon pressure of *ca.* 1 mm Hg and about 35 W for a pressure of *ca.* 5 mm Hg. The argon lines were quite weak in intensity and the argon:antimony line intensity ratio decreased with increasing power ratings.

Atomic-fluorescence measurements

A $10^{-3}M$ solution of antimony was nebulized into both air–acetylene and air–propane flames. Under optimum conditions both flames gave similar fluorescence

signals, but because of its much lower background radiation the air–propane flame was selected for more detailed study (both background and fluorescence signals are recorded together under the conditions of measurements[5]). The fluorescence readings shown in Table I were obtained under the optimum conditions. As can be seen the "forbidden" intercombination lines ($^4P \rightarrow {}^2D$ transitions) fluoresce relatively strongly.

TABLE I.—ATOMIC-FLUORESCENCE MEASUREMENTS AT 0·05 mm SLITWIDTH

Spectral line, Å	Transition	Relative fluorescence signal
2068	$^4S_{1\frac{1}{2}} \rightarrow {}^4P_{2\frac{1}{2}}$	57
2176	$^4S_{1\frac{1}{2}} \rightarrow {}^4P_{1\frac{1}{2}}$	80
2311	$^4S_{1\frac{1}{2}} \rightarrow {}^4P_{\frac{1}{2}}$	108
2511	$^4P_{2\frac{1}{2}} \rightarrow {}^2D_{1\frac{1}{2}}$	0
2598	$^4P_{2\frac{1}{2}} \rightarrow {}^2D_{2\frac{1}{2}}$	52
2671	$^4P_{1\frac{1}{2}} \rightarrow {}^2D_{1\frac{1}{2}}$	10
2770	$^4P_{1\frac{1}{2}} \rightarrow {}^2D_{2\frac{1}{2}}$	25
2878	$^4P_{\frac{1}{2}} \rightarrow {}^2D_{1\frac{1}{2}}$	35

This effect was not so marked in our previous study of selenium and tellurium,[9] probably because with antimony the absorption process is by an "allowed" line, but with selenium and tellurium both absorption and fluorescence are "forbidden". This type of fluorescence can be used with advantage to eliminate flame and particle light-scattering if it occurs, *e.g.*, with a total-consumption aspirator-burner. If a filter which transmits radiation only below *ca.* 2400 Å is placed between the source of excitation and the flame and fluorescence measurements are made at 2598, 2671, 2770, or 2878 Å, then light-scattering interference cannot occur.

The fluorescence intensity at the 2598·09 Å line ($^4P_{2\frac{1}{2}} \rightarrow {}^2D_{2\frac{1}{2}}$) is considerably greater than that at the 2671 Å ($^4P_{1\frac{1}{2}} \rightarrow {}^2D_{1\frac{1}{2}}$), 2770 Å ($^4P_{1\frac{1}{2}} \rightarrow {}^2D_{2\frac{1}{2}}$) and the 2878 Å ($^4P_{\frac{1}{2}} \rightarrow {}^4D_{1\frac{1}{2}}$) lines (*cf.* Table I). This was unexpected as the wavelength for excitation, 2068 Å ($^4S_{1\frac{1}{2}} \rightarrow {}^4P_{2\frac{1}{2}}$), is not the strongest line for absorption. In addition, from Sommerfield's intensity rule, the $^4P_{2\frac{1}{2}} \rightarrow {}^2D_{2\frac{1}{2}}$ transition intensity would be expected to be less than that of the $^4P_{1\frac{1}{2}} \rightarrow {}^2D_{2\frac{1}{2}}$ and $^4P_{\frac{1}{2}} \rightarrow {}^2D_{1\frac{1}{2}}$ transitions, and also the photomultiplier response is more sensitive at the longer wavelengths. This implies that the fluorescence signal given at 2598 Å is due to an effect other than, or in addition to, "direct-line" fluorescence. This can be explained if it is assumed that the fluorescence signal given at 2598 Å is "direct-line" fluorescence from the 2598·09 Å line ($^4P_{2\frac{1}{2}} \rightarrow {}^2D_{2\frac{1}{2}}$) plus a fluorescence signal from the nearby, unresolved, 2598·05 Å line ($^2P_{\frac{1}{2}} \rightarrow {}^2D_{1\frac{1}{2}}$). The $^2P_{\frac{1}{2}}$ state lies only 0·13 eV above the $^4P_{1\frac{1}{2}}$ state (the $^4S_{1\frac{1}{2}} \rightarrow {}^4P_{1\frac{1}{2}}$ transition line gives the greatest absorption) and some of the excited atoms in the $^4P_{1\frac{1}{2}}$ state could be thermally excited to the $^2P_{\frac{1}{2}}$ state. This is a radiationless transition and the $^2P_{\frac{1}{2}} \rightarrow {}^2D_{1\frac{1}{2}}$ transition is a spin-allowed transition favoured by Sommerfield's intensity rule.

This type of fluorescence, which can be called thermally-assisted direct line fluorescence, does not appear to have been reported before. In this particular instance, because of the nearness of the two lines, it was not possible for us to come to a more definite conclusion. However, we have observed the same effect in studying the fluorescence of bismuth atoms and in this instance the effect has been proved conclusively. These results will be reported at a later date.

Linear calibration curves were obtained for aqueous solutions of antimony over the range 10^{-6}–10^{-3}M (*ca.* 0·1–120 ppm), the 2176 Å resonance line being used. The limit of detection in water (signal:noise ratio = 1) was 5×10^{-7} *M* (0·05 ppm). The sensitivity can be increased substantially by nebulizing with organic solvents to increase the volume of solution reaching the flame[9] (*ca.* 5-fold increase) and by modulating the light source to eliminate all background radiation. Greater sensitivity may be obtained at 2311 Å, but this wavelength was not used in this study because of a "light leak" in the monochromator at *ca.* 2300 Å and because it was desired to make a direct comparison with atomic-absorption measurements with the same source. The 2176 Å resonance line gives the strongest absorption signal and in theory should, therefore, give the strongest fluorescence signal. This does not happen here because the photomultiplier (EMI 9601B) is less sensitive at 2176 Å than at 2311 Å. The limit of detection quoted could therefore be considerably improved with better instrumentation.

The variation in the fluorescence signal of an acidic 10^{-4} *M* antimony solution caused by 10^{-2} *M* Cd, Co(II), Cu(II) Fe(II), Hg(II), K, Mg, Mn(II), Mo(VI), Na, NH_4, Pb, Zn, arsenate, chloride, nitrate, phosphate and sulphate was less than 5%. The interference of other ions was not examined, but there is no reason to suppose that they would interfere.[5,10]

Atomic-absorption measurements

An air–acetylene flame was used as it gave a more stable flame than air–propane on the 7-cm burner supplied with the instrument. Also, the background is relatively unimportant in these measurements as the source is placed in the usual position for absorption on the SP900A and is therefore mechanically modulated.[5] The source was placed slightly out of focus to prevent too much light reaching the photomultiplier. As with fluorescence measurements, the optimum flame verged on luminosity. The optimum burner height was with the top of the burner head approximately 1 mm above the bottom of the monochromator slit. Table II shows the absorbance measurements obtained at the three resonance lines with 10^{-3} *M* antimony.

TABLE II.—ATOMIC-ABSORPTION MEASUREMENTS AT ~0·005 mm SLITWIDTH

Spectral line, Å	Signal absorbance
2068	0·368
2176	0·515
2311	0·247

The 2176 Å line gave the strongest absorption, and linear calibration curves over the range 5×10^{-5}–10^{-3} *M* (6—120 ppm) antimony were obtained at this wavelength. The limit of detection (1% absorbance) was 10^{-5}*M* (1·2 ppm)

The non-resonance line at 2179 Å was completely resolved from the 2176 Å line at these small slitwidths and was found not to absorb. This illustrates one of the great advantages of using an electrodeless discharge tube instead of a hollow-cathode lamp. With the latter, large slitwidths must be used because of the weak intensity of the 2176 Å line, resulting in non-resolution of the 2176 and 2179 Å lines and hence non-linear calibration curves, narrow working range, low limits of sensitivity, noise, *etc.*

As observed in our former studies[9] the atomic-fluorescence sensitivities are at least an order of magnitude better than those obtained by atomic-absorption.

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Zusammenfassung—Die Atomfluoreszenz von Antimon kann man in einer Luft-Propan-Flamme erzeugen, in der wäßrige Lösungen von Antimonsalzen versprüht sind, indem man die Flamme mit einer durch Mikrowellen erregten elektrodenlosen 30 W-Entladungsröhre bestrahlt. Die stärkste Fluoreszenz zeigt die Resonanzlinie $^4S_{1\frac{1}{2}} \rightarrow {}^4P_{1/2}$ bei 2311 Å; schwächere Signale beobachtet man bei den Resonanzlinien 2068 und 2176 Å sowie bei vier Interkombinationslinien bei 2598, 2671, 2770 und 2878 Å. Um die sonst unerklärliche Intensität der Emission bei 2598 Å zu erklären, wird eine thermisch unterstützte direkte Fluoreszenz postuliert. Atomfluoreszenz-Spektroskopie bei 2176 Å gestattet die Bestimmung von Antimon von 0,1–120 ppm mit einer Nachweisgrenze von 0,05 ppm. Mit derselben Apparatur und Lichtquelle war der Meßbereich bei Atomabsorption 6–120 ppm und die Nachweisgrenze 1 ppm. 100-fache molare Überschüsse von Cd, Co, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, NH_4, Pb, Zn, Arsenat, Chlorid, Nitrat, Phosphat und Sulfat störten nicht merklich.

Résumé—On peut engendrer la fluorescence atomique de l'antimoine dans une flamme air-propane en nébulisant des solutions aqueuses de sels d'antimoine pendant qu'on irradie la flamme au moyen d'un tube à décharge sans électrode excité par ondes courtes et opérant à 30 W. La plus forte fluorescence est manifestée par la raie de résonance $^4S_{1\frac{1}{2}} \rightarrow {}^4P_{\frac{1}{2}}$ 2311 Å et des signaux plus faibles sont observés aux raies de résonance 2068 et 2176 Å et à quatre raies d'intercombinaison, à 2598, 2671, 2770 et 2878 Å. On admet un processus de fluorescence de raie directe thermiquement assisté pour interpréter l'intensité autrement inexplicable de la raie d'émission 2598 Å. La spectroscopie de fluorescence atomique à 2176 Å permet le dosage de l'antimoine dans le domaine 0,1–120 p.p.m. avec une limite de détection de 0,05 p.p.m. Avec les mêmes équipement et source, le domaine de mesure pour l'absorption atomique a été de 6–120 p.p.m. et la limite de détection de 1 p.p.m. On n'a pas observé d'interférences avec des quantités molaires 100 fois plus grandes de Cd, Co, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, NH_4, Pb et Zn ou avec l'arséniate, le chlorure, le nitrate, le phosphate et le sulfate.

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EIN SCHNELLVERFAHREN ZUR RHENIUMBESTIMMUNG IN MOLYBDÄNIT

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Zusammenfassung—Es wird eine neue Methode für die Bestimmung des Rheniums in Molybdänit beschrieben. Es wird eine Extinktions-Verhältnis-Methode angewendet, durch die das Rhenium als Thiocyanatokomplex, auch bei Anwesenheit von Molydbän ohne vollständige Trennung, bestimmt werden kann.

DIE spektralphotometrische Bestimmung von Rhenium in Erzen wird durch die Anwesenheit von Molybdän stark gestört, besonders die sehr genaue und empfindliche Bestimmung als Thiocyanatokomplex. Bei allen herkömmlichen spektralphotometrischen Methoden muß deshalb diese Störung durch geeignete Trennverfahren ausgeschaltet werden. Durch den hierfür nötigen Aufwand ist diese Methode nicht für schnelle, serienmässige Bestimmungen geeignet.[1–6]

GRUNDLAGEN

Aus dem Vergleich der Absorptionspektren der Thiocyanatokomplexe von Rhenium und Molybdän[7,8] geht hervor, daß die "Extinktions Verhältnis-Methode"[9] anwendbar ist.

Die Konzentration C an Rhenium in einer Lösung die Rhenium und Molybdän enthält, läßt sich durch folgende Formel berechnen:

$$C = \frac{E' - RE''}{B} \tag{1}$$

E' = Summenextinktion bei der Wellenlänge λ', E'' = Summenextinktion bei der Wellenlänge λ'', die Konstante R wird an einer reinen Molybdänlösung ermittelt:

$$R = E_{Mo}'/E_{Mo}'' \tag{2}$$

Hier E_{Mo}' bzw. E_{Mo}'' = Extinktion bei der Wellenlängen λ', λ''. Die Konstante B ergibt sich durch Umformung von (1):

$$B = \frac{E' - RE''}{C} \tag{3}$$

Sie läßt sich aus einer Lösung mit bekannter Rhenium-Konzentration C bestimmen.

Bei dieser Extinktions-Verhältnis-Methode ist eine vollständige Trennung von Rhenium und Molybdän nicht erforderlich. Man muß lediglich den Molybdängehalt der Lösung auf eine gewisse Grenze herabsetzen und anschließend die Extinktionen bei zwei geeigneten Wellenlängen ermitteln. Nach (1) läßt sich der Rheniumgehalt der Lösung berechnen. Die Konstanten R und B müssen vorher experimentell bestimmt werden.

EXPERIMENTELLER TEIL

Apparate

Beckman Spektralphotometer, Modell DU Tpy 2400 mit SEV-Zusatz. Schüttelapparat (Eigenfabrikat), 4 Pulsschläge pro Sekunde.

Reagenzien

Alle Reagenzien *p.a.* der Firm Hopkin and Williams, oder Merck AG.

Rhenium, 1 mg/ml:[5] 100 mg Metallpulver werden in 50 ml Wasser suspendiert und mit Chlorgas oxydiert. Überschüssiges Chlor wird durch Kochen ausgetrieben und nach Abkühlen wird die Lösung mit Wasser auf 100 ml aufgefüllt.

Molybdän, 1 mg/ml: 1,500 g Molybdäntrioxyd werden in 100 ml 5% iger Natronlauge gelöst und auf 1000 ml aufgefüllt.

Wolfram, 1 mg/ml: 1,794 g Natriumwolframat (Na_2WO_4) werden in 500 ml Wasser gelöst und auf 1000 ml aufgefüllt.

TPA, 0,05*M*: 21,0 g Tetraphenylarsoniumchlorid (TPA) werden in Wasser gelöst, und auf 1000 ml aufgefällt.

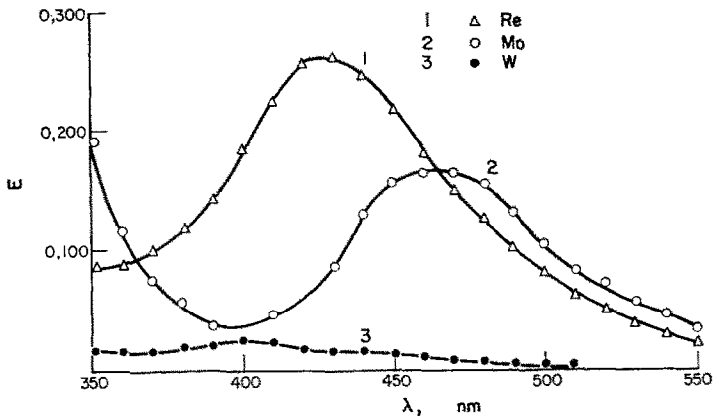

ABB. 1.—Absorptionsspektren der Thiocyanatokomplexe von Re bzw. Mo bzw. W in Isoamylalkohol.

Absorptionsspektren

Für die Auswahl der beiden Meßwellenlängen werden die Absorptionsspektren von Isoamylalkohol Extrakten ermittelt, die je 2 μg Rhenium bzw. Molybdän bzw. Wolfram pro ml enthalten. Das zuletzt genannte Metall ist meistens neben Rhenium in den Erzen enthalten und bildet auch gefärbte Thiocyanatokomplexe.

Arbeitsmethode

Zehn ml einer Lösung, die jeweils 50 μg Rhenium bzw. Molybdän bzw. Wolfram enthält, werden in einem 50-ml Scheidetrichter mit 0,5 ml 20%iger Natriumthiocyanat und 0,2 ml 35%iger Zinn(II)chlorid in konzentrierter Salzsäure versetzt und gut gemischt. Darauf gibt man 10 ml Isoamylalkohol hinzu, schüttelt 1 Minute im Schüttelapparat und trennt nach 2–3 Minuten Stehenlassen die wässrige Lösung in einen zweiten Scheidetrichter ab. Die organische Phase wird in einen Meßkolben von 25 ml Inhalt überführt. Der wässrige Teil wird nochmals mit 5 ml Isoamylalkohol ausgeschüttelt. Alle Extrakte werden im Meßkolben vereinigt und mit Isoamylalkohol auf 25 ml ergänzt. Die Absorptionsspektren der auf diese Weise erhaltenen Lösungen werden gegen Isoamylalkohol als Blindlösung aufgenommen und sind in Abb. 1 gegeben.

Die ausgewählte Wellenlängen sind $\lambda' = 430$ mμ (Max. für Rhenium) und $\lambda'' = 470$ mμ (Max. für Molybdän). Die Extinction von Wolfram kann im Vergleich zu den anderen beiden Elementen vernachlässigt werden, zumal der Gehalt an Wolfram in Molybdänit-Konzentration geringer als der an Rhenium ist. Ist der Gehalt an Wolfram wesentlich größer, kann die gleiche Methode für drei Komponenten[8] angewendet werden.

ERGEBNISSE

Ermittlung der Konstante R

Nach dem beschriebenen Verfahren wurden drei Extrakte des Molybdänkomplexes in Isoamylalkohol hergestellt und ihre Extinktion bei den ausgewählten Wellenlängen in Küvetten von 1 cm Schichtdicke gegen Isoamylalkohol gemessen (Tabelle I). Die Konstante R wird mittels Gleichung (2) berechnet.

TABELLE I.—BESTIMMUNG DER KONSTANTE R

Mo in Isoamylalkohol, *mg/ml*	E'_{Mo}, 430 *mμ*	E''_{Mo}, 470 *mμ*	R
2	0,117	0,234	$0{,}50_0$
6	0,230	0,455	$0{,}50_5$
9	0,333	0,635	$0{,}52_5$
			Mittelwert $0{,}51_0$

Ermittlung der Konstante B

Nach demselben Verfahren wurden Lösungen mit verschiedenem Gehalt an Rhenium- und Molybdän-Thiocyanatokomplex hergestellt. Der Gehalt an jedem Element im organischen Extrakt ergibt sich aus der gegebenen Menge in der wässrigen Lösung und dem Volumen an Isoamylalkohol. Die Extinktionen dieser Extrakte wurden bei den ausgewählten Wellenlängen in Küvetten von 1 cm Schichtdicke gegen Isoamylalkohol gemessen (Tabelle II). Die Konstante B läßt sich mittels Gleichung (3) berechnen.

TABELLE II.—BESTIMMUNG DER KONSTANTE B

Re in Isoamylalkohol *μg/ml*	Mo in Isoamylalkohol *μg/ml*	E' 430 *mμ*	E'' 470 *mμ*	B
1	3	0,207	0,280	0,064
1	6	0,317	0,504	0,060
1	9	0,422	0,692	0,069
2	3	0,312	0,358	0,065
2	9	0,510	0,733	0,068
3	3	0,375	0,356	0,065
			Mittelwert	0,065

Nach Einsetzen der beiden Konstanten in Gleichung (1) erhält man die Konzentration C des Rheniums im Isoamylalkohol in μg/ml:

$$C = \frac{E' - 0{\cdot}51E''}{0{\cdot}065}. \qquad (4)$$

Trennung des Rheniums von Molybdän

In einer vorliegenden Lösung von Rhenium und Molybdän kann der größte Teil des Molybdäns durch folgendes Verfahren entfernt werden: 10 ml der Versuchslösung werden in einem 50-ml Scheidetrichter mit 0,5 ml 0,05*M* TPA-Lösung versetzt und zweimal mit 10 ml Chloroform extrahiert, nachdem jeweils 2 Minuten im Schüttelapparat geschüttelt wurde. Zu den gesammelten Chloroformextrakten, die das

Rhenium enthalten, gibt man 20 ml Wasser, 0,5 ml einer 6*M* Natriumhydroxidlösung, und verdampft das Chloroform auf dem Wasserbad. Die zurückbleibende wässrige Lösung wird mit 2 ml konzentrierter Salzsäure versetzt. Neben dem Rhenium ist ein kleiner Anteil des Molybdäns in der Lösung enthalten, da etwas Molybdän-TPA-Komplex im Chloroform gelöst wird. Auch die Bildung von Emulsionen, die nur schwer zu trennen sind, trägt hierzu bei.

Spektralphotometrische Bestimmung

Die gesamte Lösung die von der Molybdän-Trennung erhalten worden ist, wird in einen 50-ml Scheidetrichter überführt und mit 0,5 ml 20% iger Natriumthiocyanatlösung und 0,2 ml 35%iger Zinn(II)chlorid in konzentrierter Salzsäure versetzt. Die Thiocyanatokomplexe werden mit Isoamylalkohol extrahiert und auf 25 ml ergänzt. Manchmal entsteht eine Trübung durch mitgeschleppter überschüssiges TPA, die durch Filtration beseitigt wird. Die Extinktionen dieser Lösung werden nun bei 430 und 470 mμ in 1-cm Küvetten gegen Isoamylalkohol als Blindlösung gemessen und der Gehalt an Rhenium nach Gleichung (4) berechnet. In der Tabelle III sind die Ergebnisse einer Reihe von Testlösungen zusammengestellt. Der Gehalt an Molybdän war allemal 1 mg/ml.

Anwendung der Methode zur Analyse von Molybdänit-Konzentraten

In einem 250-ml Becherglas werden 1,000 g Molybdänit mit 10 ml rauchender Salpetersäure versezt, mit einem Uhrglas abgedeckt und auf dem Wasserbad solange

TABELLE III.—ANALYSE VON GEMISCHEN VON RHENIUM UND MOLYBDÄN

Re		E'	E''
gegeben μg	gefunden μg	30 mμ	470 mμ
12,5	12	0,725	1,36
25,0	23	0,177	0,230
75,0	74	0,400	0,405
100,0	103	0,325	0,113
125,0	122	0,370	0,105
200,0	204	0,720	0,370

Das Gesamtvolumen des Isoamylalkoholextraktes beträgt 25 ml.

TABELLE IV.—BESTIMMUNG VON RHENIUM IN MOLYBDÄNIT

Einwaage, g	Re gefunden, %
1,000	0,048
1,000	0,050
1,000	0,052
1,000	0,050
1,000	0,053
1,000	0,052
0,765	0,052
1,190	0,051

Muster des Bureau of Mines, U.S.A. Zusammensetzung: MoS_2 95,1%, Fe 1,34%, Cu 0,5%, P 0,31%, Re, 0,05%, W < 0,001%.

erwärmt, bis keine schwarzen Teilchen übrigbleiben. Durch Zusatz von konzentrierter Salzsäure und Eindampfen auf etwa 2 ml wird die überschüssige Salpetersäure entfernt, mit 6*M* Natriumhydroxidlösung neutralisiert und mit festem Natriumhydrogenkarbonat behandelt bis die Lösung ein pH von 8–9 aufweist. Die Lösung wird in einen 100-ml Meßkolben überführt und dieser mit Wasser aufgefüllt. Dann werden 10 ml der so erhaltenen Lösung in einen 50-ml Scheidetrichter pipettiert und die spektralphotometrische Bestimmung dazu angewandt. In Tabelle IV sind die Ergebnisse zusammengestellt.

SCHLUSSFOLGERUNGEN

Die vorgeschlagene Bestimmungsmethode für Rhenium ist schneller und sicherer als die herkömmlichen und kann daher für Serienbestimmungen empfohlen werden. Die Genauigkeit der vorliegenden Methode liegt innerhalb der Grenzen einer photometrischen Bestimmung.

Summary—A new procedure is described for the spectrophotometric determination of rhenium in molybdenite. It entails the use of an absorbance-ratio method and allows the determination of rhenium in the presence of molybdenum. A great advantage over previous procedures is that it is not necessary to separate the molybdenum completely. Loss of rhenium during evaporations is prevented by use of an alkaline medium.

Résumé—On décrit une nouvelle technique de dosage spectrophotométrique du rhénium dans la molybdénite. Elle comporte l'emploi d'une méthode de rapport d'absorbance et permet le dosage de rhénium en présence de molybdène. Un grand avantage par rapport aux techniques antérieures réside dans le fait qu'il n'est pas nécessaire de séparer complètement le molybdène. On évite les pertes en rhénium durant les évaporations par l'emploi d'un milieu alcalin.

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SUR LA DÉTERMINATION DES CHALEURS DE NEUTRALISATION DE QUELQUES AMINES ALIPHATIQUES PAR LE TITRAGE ENTHALPIMÉTRIQUE

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Résumé—Dans ce travail on a effectué le titrage enthalpimétrique de quelques amines aliphatiques. On a calculé les chaleurs de neutralisation respectives à partir des données expérimentales et on a étudié la variation de la basicité de ces amines en fonction de l'accumulation des groupes alcoyles, —OH, —NH_2. Dans chaque cas on a tracé des courbes de titrage en coordonnées droites, et en coordonnées obliques pour l'élimination des effets thermiques secondaires. On constate de la sorte que l'éthylamine est plus basique que l'éthanolamine, et que la diéthylamine est une base plus forte que l'éthylamine et la triéthylamine parce que, dans ce dernier cas, intervient un facteur stérique qui entraîne une baisse de la basicité de l'amine tertiaire. La baisse de la basicité de l'éthanolamine par rapport à l'éthylamine s'explique par la présence du groupe —OH qui attire les électrons et provoque une baisse de la densité électronique dans l'atome d'azote. Bien que l'éthylènediamine contienne deux groupes —NH_2, l'un d'eux est hydraté dans la solution et l'autre protonisé. L'existence dans la molécule de l'amine protonisée du groupe —OH détermine, de par son influence négativante, une baisse de la dissociation au deuxième palier. Les éthanolamines sont des bases plus faibles que les diéthyl- et triéthylamine, par suite de la présence du groupe —OH, qui amène une diminution de la basicité de celles-ci. L'influence du facteur stérique se manifeste aussi dans le cas de la triéthanolamine; aussi celle-ci a-t-elle une basicité plus réduite que la diéthanolamine. Ces faits sont confirmés par les chaleurs de neutralisation calculées expérimentalement.

DANS un travail précédent,[1] nous avons publié les résultats du titrage enthalpimétrique de quelques amines aromatiques (les *o*-, *m*- et *p*-phénylènediamines), en étudiant l'influence réciproque de la position des deux fonctions aminées sur la basicité des trois amines.

En ce qui concerne la technique de travail, nous apportions des améliorations en utilisant, pour la détermination de la variation de température pendant la réaction, un thermistor en pont, dont la précision est de 0.001°.

Certains auteurs[2] recommandent d'utiliser une burette automatique à piston, avec écoulement continu et rapide de l'agent de titrage, et de mesurer la variation de la température, au cours du processus étudié, avec un thermistor en pont. Il semble que par l'utilisation de la burette automatique à écoulement continu et rapide, la mise en thermostat de la solution que l'on titre n'est pas nécessaire, parce que la titrage dure 10 à 20 secondes, de sorte que les effets thermiques secondaires ne sont plus enregistrés. A cet égard, nous nous permettons de considérer qu'un écoulement lent de l'agent de titrage permet de déterminer (dans le cas de réactions de neutralisation) plusiers

TABLEAU I

No.	Substance	Q	N_{m_1}	N_{m_2}	ΔT_1, °C	ΔT_2, °C
1.	Ethylamine	$0{,}304_6$	0,003712	—	0,1386	—
2.	Ethanolamine	$0{,}334_9$	0,004778	—	0,117	—
3.	Ethylènedi-amine	$0{,}334_9$	0,01125	0,01125	0,407	0,391
4.	Diéthylamine	$0{,}334_9$	0,002316	—	0,0807	—
5.	Diéthanol-amine	$0{,}334_9$	0,01206	—	0,3865	—
6.	Triéthylamine	$0{,}304_6$	0,01244	—	0,34	—
7.	Triéthanol-amine	$0{,}334_9$	0,02737	—	0,645	—

points d'équivalence, avec une précision meilleure, ce qui, du point de vue théorique et pratique, est souvent très important. Par ailleurs, l'élimination des effets thermiques secondaires, par le passage des coordonnées droites à des coordonnées obliques, est plus sûr, en particulier dans les cas où la chaleur de réaction est plus faible. Il est probable que, si l'on pouvait réaliser une amplification électronique de signal émis par le thermistor, ces précautions seraient superflues.

En outre, il convient de tenir compte du fait que dans les titrages enthalpimétriques le solvant joue un rôle important.[3] Ainsi, dans des solvants organiques, dont les chaleurs spécifiques sont basses, à de petits changements d'énergie correspondent de grandes variations de température.

Dans ce travail nous présentons et discutons les résultats obtenus lors de la neutralisation de quelques amines aliphatiques primaires, secondaires ou tertiaires. Nous y étudions l'influence qu'exercent sur la basicité de ces amines certains substituants, à savoir: —OH et $—NH_2$.

PARTIE EXPERIMENTELLE

Détermination de la constante enthalpimétrique de la cellule de titrage

La détermination de cette constante se fait par titrage enthalpimétrique d'une solution $10^{-2}M$ de l'acide chlorhydrique par une solution $10^{-1}M$ de soude. Nous avons utilisé la relation:

$$Q = N_m \frac{\Delta H}{\Delta T_Q} = 0{,}002874 \cdot \frac{13{,}4}{0{,}115} = 0{,}336 \qquad (1)$$

où:

Q est la constante enthalpimétrique de la cellule de titrage,
N_m est le nombre de moles de chlorure de sodium formés,
$\Delta H = 13{,}4$ kcal/mole,
ΔT_Q est la variation totale de température à la neutralisation de 250 ml de l'acide chlorhydrique $10^{-2}M$ par soude $10^{-1}M$.

Cette valeur de Q a été utilisée seulement pour les titrages de l'éthanolamine, de l'éthylènediamine, de la diéthylamine, de la diéthanolamine et de la triéthanolamine.

Pour les titrages de l'éthylamine et de la triéthylamine nous avons été dans l'obligation d'utiliser une autre cellule de titrage, dont la constante enthalpimétrique Q_1 a la valeur:

$$Q_1 = N_m \frac{\Delta H}{\Delta T_Q} = 0{,}002842 \cdot \frac{13{,}4}{0{,}125} = 0{,}304_6$$

TABLEAU II

No.	Substance	ΔH_1 *kcal/mole*	ΔH_2 *kcal/mole*	C, M	C_{HCl}, M
1.	Ethylamine	−11,37	—	$3 \cdot 10^{-2}$	1
2.	Ethanolamine	−8,20	—	$1{,}5 \cdot 10^{-2}$	1
3.	Ethylènedi-amine	−12,11	−11,641	$5{,}63 \cdot 10^{-2}$	1
4.	Diéthylamine	−11,67	—	$0{,}772 \cdot 10^{-2}$	0,106
5.	Diéthanol-amine	−10,73	—	$4{,}82 \cdot 10^{-2}$	1
6.	Triéthylamine	−8,32	—	$4{,}987 \cdot 10^{-2}$	1
7.	Triéthanol-amine	−7,89	—	10^{-1}	1

Titrage enthalpimétrique des amines étudiées

Pour le titrages de ces amines, tants primaires que secondaires ou tertiaires, on a préparé des solutions de concentrations comprises entre $10^{-1}M$ et $10^{-2}M$, Tableau II, que l'on a titrées par l'acide chlorhydrique $1M$, en étudiant la variation de la température pendant la neutralisation. Les données obtenues ainsi que les chaleurs de neutralisation calculées à l'aide de la relation:

$$\Delta H = \frac{Q}{N_m} \cdot \Delta T_Q \tag{2}$$

où:

ΔH est la chaleur de réaction,
Q est la constante enthalpimétrique de la cellule,
N_m est le nombre de moles de produit formé,
QT_Q est la variation de température pendant le titrage, sont consignées au tableau I,
où Q, N_{m1}, N_{m2}, ΔT_1, ΔT_2, ΔH_1, ΔH_2 ont les mêmes significations que les termes de la relation (2), C est la concentration molaire de la substance et C_{HCl} la concentration molaire de l'acide chlorhydrique employé pour le titrage.

Pour écarter les effets thermiques secondaires on a appliqué dans tous les cas une transformation des coordonnées droites en coordonnées obliques, en utilisant les relations:

$$X_{B'} = x\sqrt{1+p^2} = x \cdot \varepsilon \tag{3}$$

$$Y_{B'} = y - p \cdot x \tag{4}$$

où:

x et y sont les coordonnées droites des points B (et du point C dans le cas de l'éthylènediamine),
X et Y sont les coordonnées obliques des points B' (et du point C' pour l'éthylènediamine),
p est la pente de la dernière portion des courbes de neutralisation (les segments BC, et pour l'éthylènediamine le segment CD), en coordonnées droites. On calcule la pente au moyen de la relation:

$$p = \frac{\Delta T}{\Delta n}$$

Δn étant le volume d'acide chlorhydrique correspondant au segment BC (pour l'éthylènediamine CD), et ΔT la variation de température correspondante.

Les valeurs de ces grandeurs sont reportées au Tableau II et Tableau IV.

Dans la relation (3) on remarque que $X_{B'} = x \cdot \varepsilon$. La grandeur $\varepsilon = \sqrt{1+p^2}$ a une valeur pratiquement égale à l'unité, parce que p^2 est très petit et que, par conséquent, on peut le négliger dans tous les cas.

Afin d'expliciter les différences entre les courbes en coordonnées droites et obliques nous avons choisi les cas de l'éthanolamine (Fig. 1) et de l'éthylènediamine (Fig. 2). Dans le second la courbe révèle les deux points d'équivalence qui apparaissent lors de la neutralisation.

TABLEAU III

No.	Substance	x	y	p	$X_{B'}$	$Y_{B'}$
1.	Ethylamine	3,5	0,14	0,0004	3,5	0,139
2.	Ethanolamine	4,53	0,135	0,00400	4,53	0,117
3.	Ethylènedi-amine	8	0,391	0,00225	8	0,407
4.	Diéthylamine	21,75	0,090	0,000425	21,75	0,0808
5.	Diéthanol-amine	11,46	0,40	0,00117	11,46	0,387
6.	Triéthylamine	11,5	0,34	0	11,5	0,34
7.	Triéthanol-amine	26	0,65	0,000208	26	0,645

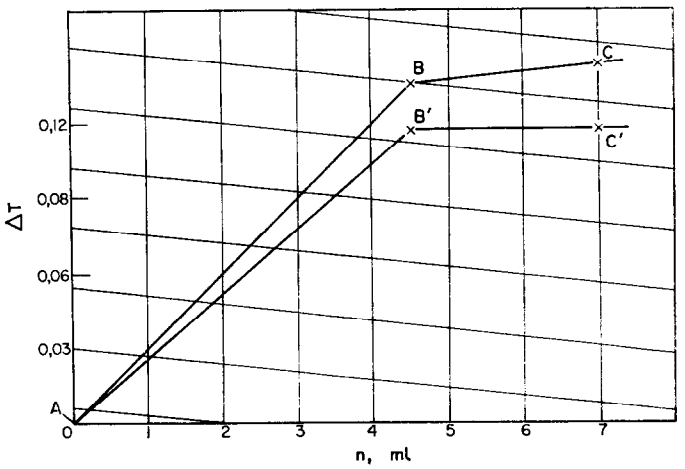

FIG. 1.

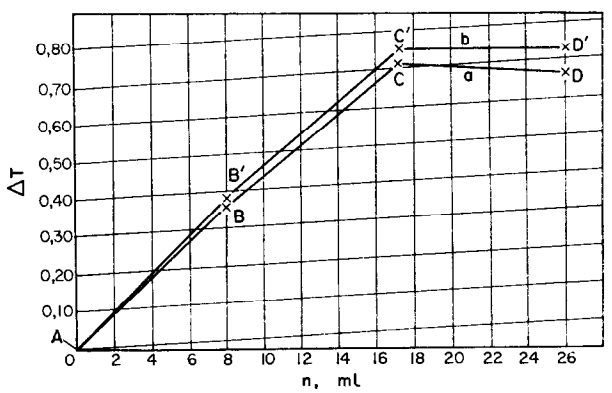

FIG. 2.

DISCUSSION

On sait que les amines aliphatiques[4] ont une basicité plus grande que l'ammoniac, par suite de leur capacité plus grande à fixer un proton. Cette capacité est due à l'effet inductif repousseur d'électrons des radicaux alcoyles,[5] qui amène un déplacement de la densité électronique vers l'azote, lorsque la mobilité du doublet libre de l'azote augmente. La chaleur de neutralisation plus grande de l'éthylamine ($\Delta H = -11{,}36$

TABLEAU IV

No.	Substance	x_C	y_C	$X_{C'}$	$Y_{C'}$
3.	Ethylènediamine	17,1	0,76	17,1	0,798

kcal/mole) confirme la basicité plus grande de celle-ci ($K_{25°} = 3{,}18 \cdot 10^{-4}$) que de l'ammoniac.

Cependant l'éthanolamine ($K_{25°} = 3{,}18 \cdot 10^{-5}$), bien que plus basique que l'ammoniac, est moins basique que l'éthylamine, ce qui ressort aussi sa chaleur de neutralisation moindre ($\Delta H = -8{,}20$ kcal/mole). Cette baisse de la basicité est due au groupe HO (attracheur d'ions), qui amène une baisse de la densité électronique à l'azote, diminuant sensiblement l'éffet inductif repousseur d'électrons du radical éthyle.

L'éthylendiamine est une base plus faible que l'éthylamine ($K_{1_{22°}} = 7{,}9 \cdot 10^{-5}$ et $K_{2_{22°}} = 7{,}9 \cdot 10^{-8}$). Dans ce cas a lieu la solvatation de l'une des fonctions amino et la protonisation de la deuxième:

$$H_2N—CH_2—CH_2—NH_2 + 2H_2O \rightarrow (HONH_3—CH_2—CH_2—NH_3)^+ + HO^-$$

La neutralisation aux deux paliers a lieu comme suit au premier palier, ou neutralise l'ion HO^-, résultant de la protonation de la base:

$$(HONH_3—CH_2—CH_2—NH_3)^+ + HO^- + (H^+ + Cl^-) = (HONH_3—CH_2—CH_2—NH_3)^+ + Cl^- + H_2O$$

et au second palier l'hydroxyle de la fonction amino solvatée:

$$(HONH_3—CH_2—CH_2—NH_3)^+ + Cl^- + (H^+ + Cl^-) = (NH_3—CH_2—CH_2—NH_3)^{2+} + 2Cl^- + H_2O$$

La dissociation au deuxième palier est diminuée par la présence de l'ion HO^- dans la molécule de l'amine protonisée. Mais au cours du titrage du deuxième palier, par la fixation de l'ion HO^- de la fonction amino solvatée sous forme de molécule d'eau non dissociée, l'équilibre de dissociation se déplace vers la droite, ce qui explique la chaleur de neutralisation également importante au deuxième palier ($\Delta H_1 = -12{,}1$ kcal/mole et $\Delta H_2 = -11{,}6$ kcal/mole). La différence entre les chaleurs de neutralisation aux deux paliers confirme la différence de basicité des deux fonctions amino.

Dans le cas des amines secondaires et tertiaires, la basicité croît avec l'augmentation du nombre et de la grandeur des substituants. C'est ce qui explique pourquoi la diéthylamine ($K_{25°} = 8{,}57 \cdot 10^{-4}$) et la triéthylamine ($K_{25°} = 5{,}66 \cdot 10^{-4}$) sont plus basiques que l'éthylamine. Par ailleurs, la diéthylamine ($\Delta H = -11{,}7$ kcal/mole) est une base plus forte que la triéthylamine ($\Delta H = -8{,}3$ kcal/mole). Cette baisse de la basicité des amines tertiaires par rapport aux amines secondaires est due tant à un effet stérique,[6] qui s'oppose à la formation de l'ion d'ammonium (en diminuant la basicité de l'amine tertiaire), qu'à la diminution de la capacité de solvatation, laquelle, comme on le sait déjà est moindre chez les amines tertiaires que chez les amines secondaires. La baisse de la capacité de solvatation de l'ion d'ammonium amène une baisse de la stabilité de celui-ci et inversement.

Enfin, les diéthanolamines et les triéthanolamines sont des bases plus faibles que

les diéthyl et triéthylamines correspondantes en raison de l'accumulation des groupements hydroxylés et des causes mentionnées ci-dessus. D'ailleurs les chaleurs de neutralisation de la diéthanolamine ($\Delta H = -10{,}72$ kcal/mole) et de la triéthanolamine ($\Delta H = -7{,}88$ kcal/mole) confirment ce fait.

Summary—Some aliphatic amines have been titrated enthalpimetrically. The heats of neutralization have been calculated from the results and correlated with the basicity of the amines and the number of hydroxyl and amine groups present. The titration curves were all plotted on Cartesian coordinates and again on oblique coordinates to eliminate secondary thermal effects. The order of basicity is ethylamine < ethanolamine, and ethylamine < diethylamine > triethylamine, the last because of steric factors reducing the basicity of the tertiary amine. The low basicity of ethanolamine relative to ethylamine is atttributed to the inductive effect of the hydroxyl group. Ethylenediamine contains two amino groups, one of which is hydrated in solution and the other protonated; the existence of the protonated group together with the electron-withdrawing power of the hydroxyl group accounts for the lower second dissociation. The ethanolamines are more feeble bases than di- and triethylamine, because of the presence of the hydroxyl group. A steric factor further reduces the basicity of triethanolamine. These facts are confirmed by the experimental heats of neutralization.

Zusammenfassung—Einige aliphatische Amine wurden enthalpimetrisch titriert. Aus den Ergebnissen wurden die Neutralisationswärmen berechnet und die Anzahl der anwesenden Hydroxyl- und Aminogruppen sowie die Basizität der Amine damit in Beziehung gesetzt. Die Titrationskurven wurden alle auf cartesischen und auf schiefen Koordinaten gezeichnet, um sekundäre thermische Effekte auszuschalten. Die Basizitätsreihenfolge ist Äthylamin > Ätholamin und Äthylamin < Diäthylamin > Triäthylamin, das letzte, da sterische Faktoren die Basizität des tertiären Amins reduzieren. Die niedrige Basizität von Äthanolamin gegenüber Äthylamin wird dem induktiven Effekt der Hydroxylgruppe zugeschrieben. Äthylendiamin enthält zwei Aminogruppen, von denen die eine in Lösung hydratisiert und die andere protoniert ist; die Existenz der protonierten Gruppe zusammen mit der elektronensaugenden Hydroxylgruppe erklärt die schwache Dissoziation in zweiter Stufe. Die Äthanolamine sind schwächere Basen als Di- und Triäthylamin wegen der Hydroxylgruppe. Ein sterischer Einfluß reduziert die Basizität von Triäthanolamin weiter, was durch die gemessenen Neutralisationswärmen bestätigt wird.

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CHROMATOGRAPHIC LOCATION AND COLORIMETRIC DETERMINATION OF MERCAPTANS, PROLINES AND FREE RADICAL PRECURSORS

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Summary—A new reagent, 7, 7, 8, 8-tetracyanoquinodimethan (TCNQ), is introduced for the colorimetric determination of free radical precursors, such as cysteine, proline, hydroxyproline, the phenoxazine family and mercaptans. TCNQ is also useful in the location and characterization on paper or thin-layer chromatograms of proline, hydroxyproline, cysteine, polynuclear compounds, mercaptans, thiocarbonyl amides and thiosemicarbazones. In addition, amino-acid derivatives, such as the *N*-(phenylthiocarbamyl) amino-acids and the 3-phenylthiodantoins, can be located and characterized on chromatograms. TCNQ has been applied to the location and characterization of atmospheric proline, carbazole and 11*H*-benzo[*a*]carbazole. For characterization purposes absorption spectra were obtained directly from glass-fibre, paper, or thin-layer chromatograms from about 300 to 900 mμ.

7,7,8,8-TETRACYANOQUINODIMETHAN is known to react readily with inorganic and organic bases to form free radicals and with polynuclear compounds to form π complexes.[1,2] Because of this reactivity we believed that this reagent could be used to analyse mixtures for compounds from which a free electron could be readily extracted, *i.e.*, free radical precursors. Thus, in this type of reaction three analytically useful phenomena could take place. A cationic free radical (from the test substance) and an anionic one (from the reagent) could be formed. The cationic free radical could dimerize, leaving the anionic free radical in solution. The third possibility would be the combination of the cationic and anionic free radicals followed by subtraction of hydrogen cyanide from the molecule to give a highly coloured zwitterion resonance structure. In addition, the test substance and the reagent could combine to form a π complex.

Examples of all these types are discussed. The application of some of the techniques to air pollution studies is described.

EXPERIMENTAL*

Reagents and apparatus

All standards were obtained in the purest form available from commercial sources and were crystallized to give a constant melting point if their physical properties indicated they were impure. 7,7,8,8-Tetracyanoquinodimethan (TCNQ) was obtained from E. I. DuPont de Nemours and Co., Wilmington, Delaware. Pyridine and 2-butanone were obtained in chemically pure form and used directly. 2,4,7-Trinitrofluoren-$\Delta^{9,\alpha}$-malononitrile was prepared by a known procedure[3] and crystallized from toluene.

* Mention of commercial products does not constitute endorsement by the Public Health Service.

Location reagent I: 0·3% TCNQ in acetone; location reagent II: 0·3% TCNQ in pyridine-acetone (1:1).

Colorimetric reagent: 0·02% TCNQ in 2-butanone. This reagent was stable for 3–4 hr.

Colorimetric analyses were accomplished with a Cary Model 11 recording spectrophotometer with 1-cm path-length cells. Direct spectrophotometric examinations of coloured spots on various adsorbents, on glass-fibre papers, and on paper and thin-layer chromatograms were performed with a Model 1411 diffuse reflectance accessory with integrating sphere mounted on a Model 14 Cary recording spectrophotometer.

Location procedure for various chemicals on a chromatogram

Spray the chromatogram with either location reagent I or II. Place the chromatogram on a heated metal surface kept at a temperature of ~60°. Observe the colour changes (see Table I). For some of the compounds, especially the sulphur compounds, heat is not necessary. In some cases, the colours are different according to whether the plate is heated or not. For example, *N,N'*-tetramethylbenzidine gives a violet colour changing to blue; when the spot is warmed, immediately after spraying, the violet colour changes quickly to a dark green.

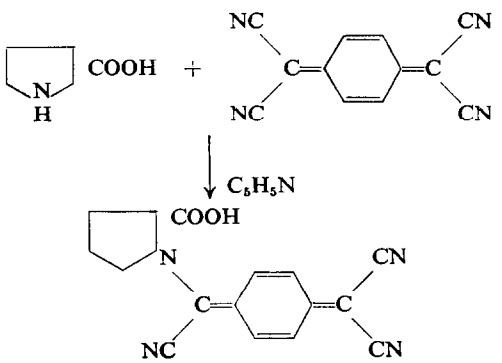
Colorimetric procedure

To 2 ml of a water–pyridine (1:1) test solution add 2 ml of 0·02% TCNQ solution in 2-butanone. Heat for 3 min at 60°. Cool under the tap and read the absorbance at 756 or 848 mμ within 3 min (see Table II).

DISCUSSION

Mechanism

Comparison of the colours obtained in location and in colorimetric analysis indicates that the predominant chromogen formed in location methods is a brilliantly coloured zwitterion resonance structure. Thus, proline reacts with TCNQ on a chromatogram in the following manner.



Purple, λ_{max} 565, 612 s

This reaction is compatible with the known reaction of pyrrolidine with TCNQ to form purple solutions of 7-pyrrolidino-7,8,8-tricyanoquinodimethan, λ_{max} 532, 567, and 613 mμ with the prominent band at 567 mμ.[2]

In the colorimetric method free radicals are formed as shown by the visible absorption spectrum obtained in the determination of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine, Fig. 1. In this case, since $Me_2N\text{-}C_6H_4\text{-}\dot{N}Me_2^+$ absorbs at 610 mμ with a molar absorptivity of 11,500,[4] and $TCNQ^{\cdot-}$ absorbs at 842 mμ with a molar absorptivity of 43,300,[1] almost quantitative yields of these radicals are obtained. Examples of many other compounds that can be determined because of their ability to donate an electron to TCNQ are given in Table II. The two bands in the near-infrared region show the approximate relation $A_{847} = 1{\cdot}86\,A_{748}$ for the absorbances.

TABLE I.—COLOURS* AND LOCATION LIMITS ($\mu g/cm^2$) OF SOME AMINO-ACIDS, MERCAPTANS, AND POLYNUCLEAR COMPOUNDS†

Compound‡	Al_2O_3 on GFP	Cellulose (TLC)		Paper	
Proline	P(0·2)	¶	P(0·7)	P(6)	P(0·1)
Thiazolidine-4-carboxylic acid	B(10)	¶	P(7)	¶	P(6)
4-Hydroxyproline	P(2)	¶	P(0·7)	P(6)	P(0·1)
Azetidine-2-carboxylic acid	P(1)	¶	P(2)	B(6)	P(0·5)
Pipecolic acid	G(8)	¶	G(16)	G(9)	G(0·5)
Cysteine	G(1)	G(1)	G(0·1)	G(6)	G(0·1)
2-Benzoxazolethiol	B(4)	V(3)	V(0·5)	V(5)	V(3)
2-Naphthalenethiol	B(8)	B(2)	B(0·3)	B(3)	B(1)
2-Mercapto-4-amino-6-hydroxy-pyrimidine	BG(2)	G(3)	G(0·3)	G(3)	G(0·4)
Thiomalic acid	BG(10)	G(4)	G(0·5)	G(2)	G(0·5)
Dithio-oxamide	BG(2)	G(2)	G(0·1)	G(0·3)	G(0·2)
Thiobarbituric acid	G(3)	G(7)	G(2)	G(2)	G(1)
Dithiobiuret	G(0·7)	G(0·7)	G(0·4)	G(1)	G(0·5)
Thiosemicarbazide	BG(5)	G(0·5)	G(0·3)	G(0·3)	G(0·2)
Acetone thiosemicarbazone	B(3)	P(13)	P(2)	P(8)	B(2)
Glyoxal bis-thiosemicarbazone	B(1)	G(8)	G(2)	G(4)	G(1)
Furfural thiosemicarbazone	B(3)	P(10)	P(3)	P(7)	P(3)
5-Methyl-2-furfural-thiosemicarbazone	B(4)	P(10)	P(2)	P(7)	P(2)
5-Hydroxymethyl-2-furfural thiosemicarbazone	B(1)	G(3)	G(2)	G(5)	G(1)
Acetophenone thiosemicarbazone	B(3)	B(13)	B(2)	B(5)	P(2)
α-Naphthylthiourea	B(3)	B(10)	B(2)	B(7)	B(3)
3-Phenylthiohydantoin	BG(2)	¶	G(1)	¶	G(2)
N-(Phenylthiocarbamyl)glycine	BG(2)	¶	G(1)	¶	G(2)
Thiourea	B(0·2)	**	BG(0·2)	BG(9)	BG(0·1)
Phenothiazine	P(5)	V(3)	V(0·9)	R(0·7)	V(5)
N,N,N′,N′-Tetramethylbenzidine	B(0·5)	P(0·9)	P(0·9)	P(0·9)	P(0·3)
Malononitrile	P(0·3)	G(7)	G(1)	BG(0·1)	BG(0·1)
Carbazole††	B(0·5)	B(0·9)	P(2)	P(0·6)	P(5)
11*H*-Benzo[*a*]carbazole	G(0·5)	G(0·5)	G(0·9)	B(0·7)	G(0·7)
4*H*-Benzo[*def*]carbazole	V(0·5)	P(0·9)	P(1)	P(0·7)	P(3)
Benzo[*a*]pyrene	OR(0·5)	RO(1)	OR(2)	RO(0·7)	OR(1)
Benzo[*e*]pyrene	Bk(1)	Bk(2·5)	Bk(3)	Bk(2)	Bk(2)
Dibenzo[*b,def*]chrysene	OR(0·5)	OR(0·5)	OR(2)	OR(0·7)	OR(1)
Acridine	V(2·5)	V(4)	P(5)	P(7)	**
Benz[*c*]acridine	V(1·6)	V(0·8)	V(2)	V(3)	V(7)
Dibenz[*a,j*]acridine	P(0·8)	P(0·4)	P(3)	P(0·7)	P(3)

* B = blue, Bk = black, G = green, O = orange, P = purple, R = red and V = violet.

† Procedure is to spray the chromatogram and then to observe development of colour. Spray reagent contained 0·3% of 7,7,8,8-tetracyanoquinodimethan (TCNQ) in acetone. In the columns labelled "cellulose (TLC)" and "paper" the spray reagent contained 0·3% of TCNQ in acetone–pyridine (1:1).

‡ Negative results were obtained on alumina with 10 μg of adenine, 1,3-diphenyl-1,3-propanedione, glucose, malathion, parathion, 2,4-pentanedione. The following compounds (10 μg) gave negative colour reactions but had a green-yellow fluorescence under ultraviolet light: δ-amino-butyric acid, n-butylamine, histidine, leucine, serine, and tryptophan.

¶ Negative at 10 μg. With cellulose and paper read colour immediately and after 5 min at 60°.

** Negative at 20 μg.

†† Polynuclear compounds form colours more quickly than proline does but also fade much more quickly.

For most of the compounds the reaction is not as simple as shown in Fig. 1. For example, while the molar absorptivity of $TCNQ^{\cdot-}$ is reported as 43,300 at 842 mμ, quite a few compounds in Table II gave higher molar absorptivities at this wavelength. Phenothiazine gave a value approximately 4 times as high as the theoretical value, apparently an indication of an autocatalytic effect. In this type of molecule the NH

TABLE II.—COLORIMETRIC DETERMINATION OF MERCAPTANS, PROLINES, AND FREE RADICAL PRECURSORS

Compound	Final concentration *M*	$\varepsilon \times 10^{-3}$ 748 mμ	848 mμ
Phenothiazine	5×10^{-6}	94	174
Phenoxazine	10^{-5}	84	144
2-Chlorophenothiazine	5×10^{-6}	72	134
o-Mercaptobenzoic acid	$2{\cdot}5 \times 10^{-5}$	38	72
Phenoxazine*	10^{-5}	36	67
Cysteine	5×10^{-5}	34	64
Cysteine*	5×10^{-5}	31	58
Phenoselenazine*	5×10^{-5}	28	53
Proline	$2{\cdot}5 \times 10^{-5}$	27	50
N,N,N′,N′-Tetramethyl-*p*-phenylenediamine	5×10^{-5}	26	48
2-Naphthalenethiol	5×10^{-5}	23	43
Hydroxyproline	$2{\cdot}5 \times 10^{-5}$	23	43
Malononitrile*	$2{\cdot}5 \times 10^{-5}$	19	35
12*H*-Benzo[*b*]phenothiazine*	5×10^{-5}	18	33
3-Phenylthiohydantoin	5×10^{-5}	16	30
5-Nitro-2-benzimidazolethiol*	10^{-4}	13	25
2-Benzimidazolethiol*	10^{-4}	13	24
2-Benzoxazolethiol*	10^{-4}	12	22
6-Nitrobenzothiazole-2-thiol*	10^{-4}	9	17
3-Amino-9-ethylcarbazole†	5×10^{-5}	9	16
Glycine	$2{\cdot}5 \times 10^{-4}$	4	8
Thiazolidine-4-carboxylic acid	$2{\cdot}5 \times 10^{-4}$	3	6
α-Naphthylthiourea*	5×10^{-4}	3	5
Tetraethylammonium iodide	5×10^{-4}	2	4
Arginine	5×10^{-4}	2	3
Azetidine-2-carboxylic acid	5×10^{-4}	1	3
Methionine	5×10^{-4}	0·9	2
Thiourea	5×10^{-4}	1	2
Histidine	5×10^{-4}	0·7	1
Negative results‡			

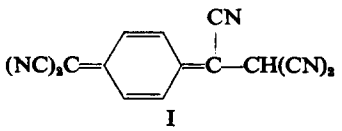
* Test run without the heating step.

† λ_{max} at 505 mμ with ε 24000.

‡ Aniline, adenine, benzo[*a*]pyrene, n-butylamine, carbazole, cytosine, 2-deoxy-D-ribose, formaldehyde, β-D-fructose, L-fucose, β-D-glucose, 9-(3-indolyl)-thioxanthene, melizitose, *o*-mercaptoaniline, *N*-phenylphenothiazine, phenyl sulphoxide, pipecolic acid, piperidine, pyrrolidine, D-ribose, D-sorbitol, *N,N,N′,N′*-tetramethylbenzidine, triethylamine, and tryptophan.

group seems to be necessary for the reaction, since *N*-phenylphenothiazine did not react.

Some of the interesting spectral results are shown in Table III. Occasionally with 3-phenylthiohydantoin a broad strong band was obtained at 630 mμ after spraying. Spectra of the coloured spots obtained from benzo[*a*]pyrene and dibenz[*a,j*]acridine were apparently derived from π complexes. With malononitrile, TCNQ reacts in solution to form a strong acid, I.[5] This compound, pK_a 0·60, ionizes readily to form a brilliantly coloured anion, λ_{max} 625 mμ, ε 52200.



I

The purple spot, λ_{max} 600 mμ, obtained on glass-fibre paper (Table III) is probably due to the coloured anion.

Location and characterization methods

Most of the methods involving the formation of π complexes with polynuclear compounds are much less sensitive than those involving the natural fluorescence of the

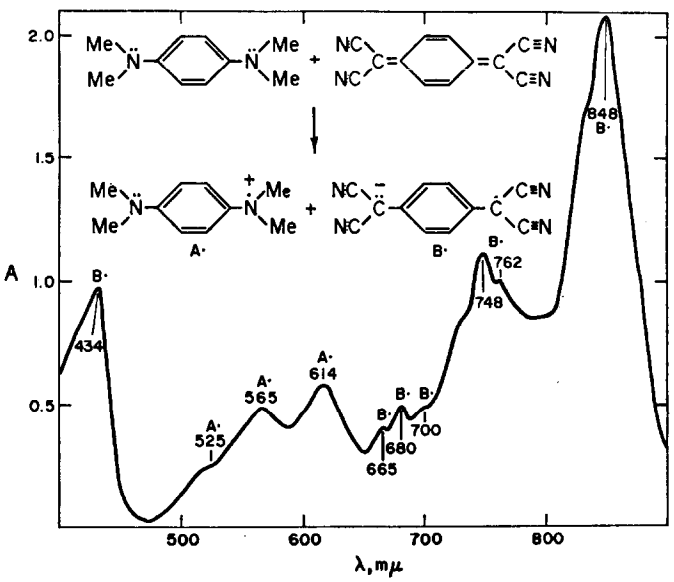


FIG. 1.—Absorption spectrum obtained in the colorimetric determination of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine ($5 \times 10^{-5}M$) with TCNQ but without heat.

molecules. Thus polynuclear compounds can be located by fluorescence on a thin-layer chromatogram in nanogram amounts[6,7] but only in microgram amounts with TCNQ. In the analysis of airborne particulates sensitivity is of vital importance. Only a few cubic metres of air are needed when it is possible to analyse for nanogram amounts of pollutant; when the method can determine only microgram amounts, then several thousand cubic metres of air are needed. Thus, the time required to collect a particulate sample for the latter type of analysis would be 100 to 1000 times as long as for a nanogram method. In many cases the colour methods are used either because the method is better or because nothing as sensitive is available.

Saturated heterocyclic imino-acids are readily located on alumina, cellulose, or paper with the help of TCNQ. The presence of pyridine in the reagent is of value in neutralizing the acidic substances present in the cellulosic absorbents. Sensitivity is better than that obtained without the pyridine. As Table I shows, brilliant colours are obtained with these compounds. Warming for about 3 min was required to develop the colours obtained with proline and hydroxyproline.

Compounds with very active hydrogen can be located readily with the reagent,

even if the hydrogen is on a carbon atom. For example, the compound obtained from malononitrile readily ionizes to give a brilliantly coloured anion, as shown by the purple to green spots obtained on the various adsorbents. Treatment of the coloured spot with trifluoroacetic acid fumes decreases the intensity of the colour, but warming the spot brings the colour back. With this treatment the dibenz[*a,j*]acridine spot loses its colour, whereas the proline spot changes from purple to a lighter red-orange.

Mercaptans can also be readily located on chromatograms. For example, cysteine gives an emerald green colour on the plate quickly and without heat.

TABLE III.—WAVELENGTH MAXIMA AND ABSORBANCES OBTAINED IN THE SPECTRAL EXAMINATION OF VARIOUS COMPOUNDS (~10 μg/cm^2) ON GLASS FIBRE-ALUMINA SPRAYED WITH TCNQ

Compound	λ_{max}*
Proline	565, 612 *s*
Hydroxyproline	565†
Cysteine	610, 440
N-(Phenylthiocarbamyl)glycine	656, 839, 825 *s*, 740, 480
3-Phenylthiohydantoin‡	839, 825 *s*, 750, 760, 735 *s*, 490, 680, 666, 440
Thiourea	625, 655, 730
Dithiobiuret	650 *br*, 830, 730
Furfural thiosemicarbazone	845, 829 *s*, 750, 760, 680, 666, 435, 480
Malonitrile	600
N,N,N',N'-Tetramethylbenzidine	650 *br*, 475, 430
Dibenz[*aj*]acridine	~575 *br*, 440
Benzo[*a*]pyrene¶	520, 450

* In order of decreasing intensity; *s* = shoulder and *br* = broad maximum.
† Spectrum obtained with help of cell space total diffuse reflectance accessory Model 1411750.
‡ Similar spectra of $TCNQ^-$ on alumina thin-layer plate.
¶ Pure benzo[*a*]pyrene gave a doublet at 367 and 385 mμ.

Compounds containing the —C(=S)—NH— group also react with the reagent, *e.g.*, thiourea, dithio-oxamide, thiobarbituric acid, dithiobiuret, and thiosemicarbazide. Thiosemicarbazones of aldehydes and ketones give brilliant colours with TCNQ on chromatograms and thus can be located in this manner. Since methods are available for the paper chromatographic separation of the thiosemicarbazones of aldehydes and ketones,[8] TCNQ could be of value in locating these derivatives. In addition the separated spots can be characterized or estimated through direct spectrophotometric examination.

Phenylthiocarbamylamino acids and phenylthiohydantoins are readily prepared from amino-acids.[9,10] These derivatives have been separated by paper[11] and thin-layer chromatography.[12] The derivatives from glycine gave positive results with the location method. Consequently, TCNQ could be used to locate and characterize these two types of amino-acid derivative on the chromatogram or phoretogram.

Substituting 2,4,7-trinitrofluoren-$\Delta^{9,\alpha}$-malononitrile for TCNQ in the location reagent presented no advantage for the location of prolines or mercaptans. This reagent was better suited for the location of polynuclear compounds through π complex formation. Thus, the following location limits and colours were obtained: dibenz[*a,j*]acridine, 2 μg, red-orange; benz[*a*]acridine, 2 μg, orange: benz[*c*]acridine, 2 μg, purple; benzo[*a*]pyrene, 2·5 μg, brown; benzo[*e*]pyrene, 2 μg, black.

Results obtained with the diffuse reflectance accessory were checked by examining the purple spot obtained when a paper chromatogram containing 1 μg of leucine was sprayed with ninhydrin. Prominent absorption maxima were obtained at 407 and 570 mμ. The same bands were obtained when an aqueous solution of leucine reacted with a ninhydrin reagent solution.

Absorption spectra obtained on glass-fibre paper from various compounds sprayed with TCNQ are shown in Table III. We found that thin-layer or paper chromatograms could also be used in direct spectral investigations. Our investigations

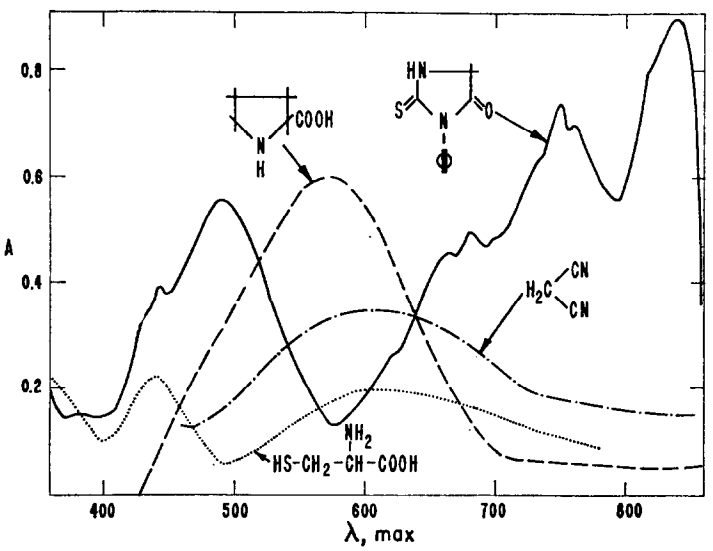


FIG. 2.—Absorption spectra obtained from glass fibre–alumina chromatograms after spraying with TCNQ location reagent.
3-Phenylthiohydantoin, 10 μg (———); proline, 10 μg (– – –); malononitrile, 10 μg (– · – · –); cysteine, 5 μg (· · ·).

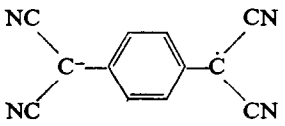
have convinced us that this technique is desirable and useful in characterizing and estimating the types of compounds studied in this paper. Examples of the spectra obtained after spraying with TCNQ are given in Fig. 2. The sensitivity could be considerably improved since only the surface of the glass fibre was stained and most of the compound was present in the sub-surface area.

Colorimetric analysis

The variables were investigated with proline as the test substance. Various solvents were tried. An aqueous pyridine mixture gave satisfactory results in dissolving a large variety of test substances and in assisting the reaction of the test substance with the reagent. Since the reagent was not readily soluble in a large variety of solvents, many solvents were investigated. 2-Butanone was satisfactory in its solvation of the reagent, its miscibility with the test solution, and its favourable influence on the test reaction. Of the various concentrations of reagent tried, 0·02% gave optimum results with the blank and the test mixture. Some heat was needed for the reaction to take place. With temperatures near 100°, the blank became too dark. Optimum results were obtained by heating at 60° for 3 min.

Conformance with Beer's law was observed from 0·8 to 12 μg of proline. The standard deviation of 11 determinations was $\pm 1{\cdot}6\%$. The colour was stable for about 10 min. In a duplicate determination average absorbances of 1·33 and 1·30 were obtained at 747 mμ when measured 3 and 20 min respectively after completion of the test.

The main chromogen formed in the determination of the compounds in Table II is the free radical anion, II.



II

The phenoxazine family of compounds gives better than theoretical (based on a 1:1 reaction) yields. Thus, the molar absorptivity obtained for phenothiazine is 4 times as great as the theoretical molar absorptivity obtained for II. These compounds can also be determined without the use of heat. Substitution of a phenyl group on the nitrogen atom of phenothiazine inhibits the reaction. As expected, the determination of phenothiazine did not conform with Beer's law.

Proline can be determined by reaction with ninhydrin;[13] hydroxyproline is usually determined by oxidation followed by reaction with *p*-dimethylaminobenzaldehyde.[14] The present procedure for these amino-acids is simpler and more sensitive but is less selective than the usual methods. Proline and hydroxyproline react well in the procedure. Except for cysteine, the other amino-acids do not react as well.

Mercaptans have usually been determined by reaction with 2,4-dinitrochlorobenzene,[15] 1,1-diphenyl-2-picrylhydrazine,[16] *N*-ethylmaleimide,[17] or bis(*p*-nitrophenyl) disulphide.[18] The present method is simpler and more sensitive for most of the compounds but is less selective. The reaction with cysteine is especially sensitive. Other types of compounds can also react, such as those with strongly active hydrogen, *e.g.*, malononitrile, and basic free radical precursors such as *N,N,N',N'*-tetramethyl-*p*-phenylenediamine.

These various reactions are complex: many compounds that react well in the location method give poor results in the colorimetric method. In addition, the type of reaction that takes place on the chromatogram is usually different from the reaction in the colorimetric procedure.

Applications

In preliminary work with this reagent we investigated some of the possibilities of its use. An urban air sample, in which coal-tar pitch fumes were the main contaminant, was separated on alumina by two-dimensional thin-layer chromatography. The location method indicated that carbazole and 11*H*-benzo[*a*]carbazole were present, Fig. 3.

A sample of airborne particulates was hydrolysed with hydrochloric acid[19] and the amino-acid fraction was then separated on a two-dimensional cellulose thin-layer plate. Spraying the chromatogram with a ninhydrin solution (0·2% in acetone containing 2% of pyridine) gave a series of violet, yellow, and orange spots (Fig. 4). The yellow spot was identified as proline on the basis of its R_f values in two different

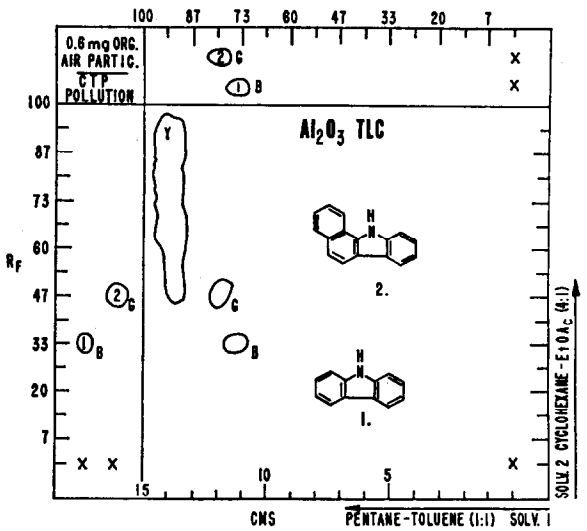


FIG. 3.—Two-dimensional alumina thin-layer chromatogram of urban airborne particulates contaminated with coal-tar pitch fumes and one-dimensional chromatograms of carbazole and 11*H*-benzo[*a*]carbazole sprayed with TCNQ location reagent.

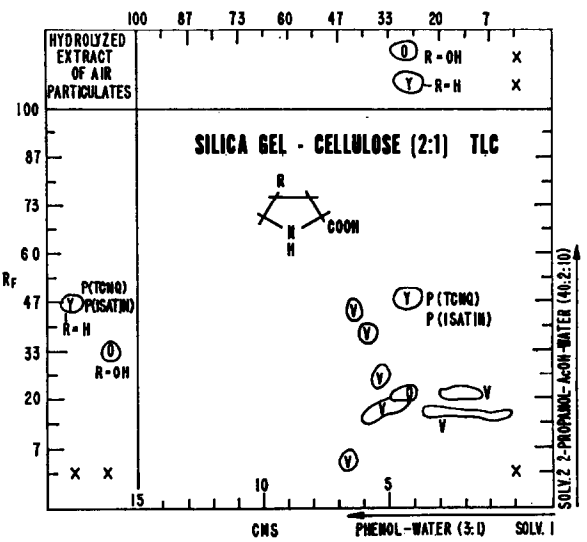


FIG. 4.—Two-dimensional silica gel–cellulose thin-layer chromatogram of an aqueous hydrolysed extract of urban airborne particulates and one-dimensional thin-layer chromatograms of proline and hydroxyproline sprayed with ninhydrin reagent.

solvent systems and its change to purple when sprayed with isatin (0·2% in acetone containing 2% of pyridine) and with TCNQ.

The amino-acid fraction was also separated on a cellulose thin-layer plate with 2-propanol–acetic acid–water (40:2:10) as the developer. Development (15-cm run) took about 3 hr. Spraying with ninhydrin gave six spots; spraying with TCNQ gave the purple spot of proline and a large emerald green spot with an R_f value close to that of cysteine. The emerald green spot has not yet been identified.

An urban airborne particulate sample was extracted with boiling water. The extract was then analysed by the colorimetric method. Based on the molar absorptivity of TCNQ $\bar{\cdot}$, 8·4 μmole of free radical precursors were found per gram of particulates.

Zusammenfassung—Zur kolorimetrischen Bestimmung von Vorläufern freier Radikale wie Cystein, Prolin, Hydroxyprolin, den Phenoxazinabkömmlingen und Mercaptanen wird ein neues Reagens, 7,7,8,8-Tetracyanochinodimethan (TCNQ) eingeführt. TCNQ ist auch von Nutzen bei Nachweis und Charakterisierung von Prolin, Hydroxyprolin, Cystein, mehrkernigen Verbindungen, Mercaptanen, Thiocarbonsäureamiden und Thiosemicarbazonen auf Papier- oder Dünnschichtchromatogrammen. Dazuhin können Aminosäurederivate wie N-(phenylthiocarbamyl)aminosäuren und 3-Phenylthiodantoine auf Chromatogrammen 10-kalisiert und charakterisiert werden. TCNQ wurde bei Nachweis und Charakterisierung von atmosphärischem Prolin, Carbazol und 11 H-benzo[*a*]carbazol verwendet. Zu Charakterisierungszwecken wurden Absorptionsspektren direkt von Glasfaser-, Papier- oder Dünnschichtchromatogrammen zwischen 300 und 900 nm aufgenommen.

Résumé—On présente un nouveau réactif, le 7,7,8,8-tétracyanoquinodiméthane (TCNQ) pour la détermination colorimétrique de précurseurs de radicaux libres comme la cystéine, la proline, l'hydroxyproline, la famille de la phénoxazine et les mercaptans. Le TCNQ est aussi utile dans la localisation et la caractérisation, sur chromatogrammes sur papier ou couche mince, de la proline, de l'hydroxyproline, de la cystéine, des composés polynucléaires, des mercaptans, des thiocarbonylamides et des thiosemicarbazones. En outre, des dérivés d'amino-acides comme les N-(phénylthiocarbamyl) amino-acides et les 3-phénylthiohydantoïnes peuvent être localisés et caractérisés sur les chromatogrammes. On a appliqué le TCNQ à la localisation et la caractérisation de la proline, du carbazole et du 11 H-benzo[*a*]carbazole dans l'atmosphère. A des fins de caractérisation, on a obtenu des spectres d'absorption directement des chromatogrammes sur fibre de verre, papier ou couche mince, d'environ 300 à 900 mμ.

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DETERMINATION OF RADIOACTIVE COBALT IN REACTOR COOLANT WATER BY SOLVENT EXTRACTION

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Summary—A rapid extraction separation method is described for the radiochemical determination of cobalt-58 and cobalt-60 in reactor coolant water. After adjustment of the pH of the sample water to 5·0–5·5, cobalt diethyldithiocarbamate is extracted with benzene. Other nuclides, *e.g.*, manganese-54 and -56, copper-64 and iron-59, which are usually present in reactor coolant water, are also extracted together with cobalt. However, they can be readily removed by washing the extract with mercury(II) chloride solution. The cobalt-58 and -60 activities are measured by gamma counting of an aliquot of the washed extract. Trace amounts of radioactive cobalt in 500 ml of sample water can be quantitatively extracted without the use of carrier. The separation could be finished in 15 min and an average recovery of 99·5% was obtained, with a relative standard deviation of 1·4% (25 experiments).

THE analysis of radioactive nuclides in the coolant water of a large power reactor is very important in many respects. It provides, for example, considerable information on the behaviour of corrosion products in the coolant, and seems to be one of the most basic means for investigating the corrosion of fuel-cladding or reactor materials. It also serves for safety monitoring of a power reactor. In the normal operation of a reactor, cobalt-58 arising from the (n, p) reaction on nickel-58 and cobalt-60 from the (n, γ) reaction on cobalt-59 are the major long-lived activities in the coolant water. A rapid and reliable method of determination of radioactive cobalt in the coolant water is therefore needed.

The standard method[1] for determination of radioactive cobalt is based on precipitation of potassium cobaltinitrite. Although this method is accurate, it is troublesome and time-consuming.

Bode *et al.*[2,3] have reported studies on the extraction of metal diethyldithiocarbamates. In their experiments, the behaviour of cobalt was found to be exceptional in that cobalt diethyldithiocarbamate is very stable. Přibil *et al.*[4] and Stolyarov[5] used this property in the photometric determination of microgram quantities of cobalt with sodium diethyldithiocarbamate; interfering metals were exchanged with mercury(II) ion, which has the highest affinity for diethyldithiocarbamate.

In the present paper, a new method based on the solvent extraction of cobalt diethyldithiocarbamate is proposed for the determination of radioactive cobalt. By this method, radioactive cobalt can be separated quantitatively, without use of a carrier, from even 500 ml of water sample containing other radioactive nuclides, and the separated cobalt nuclides are found to be radiochemically pure.

EXPERIMENTAL

Apparatus

Gamma-ray scintillation counter and spectrometer. A gamma-ray scintillation counter with a 256 channel pulse-height analyser and a well-type NaI(Tl) crystal 1¾ in. × 2 in. was used.

Reagents

Cobalt-60 tracer solution. One mg of cobalt metal, irradiated for 130 hr with about 2×10^{13} n/cm²/sec in a reactor (JRR-2), was dissolved in hydrochloric acid and the solution was diluted with water to give an activity of about 1 μCi/ml.

Standard cobalt-60 solution. Cobalt(II) chloride solution (ORNL, U.S.A.) with a certified specific activity of 54545 mCi/g of cobalt, was diluted to give a solution containing $1{\cdot}87 \times 10^{-11}$ g of cobalt per ml.

Other radioactive nuclide solutions. Each metal was irradiated in JRR-2 then dissolved in an appropriate acid: the solutions were suitably diluted with water.

Buffer, pH 5·3. About 800 ml of 1*M* ammonium acetate mixed with 200 ml of 1*M* acetic acid.

Sodium diethyldithiocarbamate solution 2%. The solution was prepared fresh daily and filtered if necessary.

Mercury(II) chloride solution, 0·05*M*. The pH of this solution was adjusted to about 3·5 with ammonium acetate.

Procedure

A sample of coolant water was filtered under suction through a Millipore filter (pores 0·45 μ). The solid remaining on the filter was ashed along with the filter in a platinum crucible; the ash was fused with 0·5 g of potassium bisulphate, and the cooled melt was dissolved in 2 ml of 6*M* hydrochloric acid and the solution was diluted to 50 ml with water.

Appropriate aliquots of the filtrate and of the residue solution were taken in separatory funnels. Up to 500 ml of sample filtrate could be used when the sample contained small amounts of radioactive cobalt. The pH of the filtrate sample was adjusted to 5·0–5·5 by addition of buffer solution (the volume usually needed was about 1/50 of the sample volume). The pH of the residue solution was adjusted to 5·0–5·5 with 5 ml of 1*M* ammonium acetate and some dilute ammonia solution.

Then 5 ml of 2% sodium diethyldithiocarbamate solution were added to the solution and the mixtures was shaken for 2 min with exactly 10 ml of benzene. The aqueous layer was discarded, 20 ml of mercury(II) chloride solution were added, and the mixture was shaken for 2 min. An exact 5-ml portion of the benzene layer was taken in a polyethylene tube, and its gamma activity was measured.

A gamma-ray scintillation spectrometer was used to resolve the 0·51-MeV positron annihilation radiation from cobalt-58 and the 1·17- and 1·33-MeV gamma rays from cobalt-60. A peak-integration technique or a spectrum stripping technique was used to estimate the amount of each isotope.

RESULTS AND DISCUSSION

Selection of organic solvent

Cobalt(III) diethyldithiocarbamate can be extracted by many organic solvents such as chloroform, carbon tetrachloride and benzene. In the procedure described above, benzene was used as the solvent for the following reasons: the specific gravity of benzene is lower than that of water, so extraction and washing can be done in the same separatory funnel; its solubility in water is very low; the volume change of benzene after equilibration is negligible even when the extraction is made from 500 ml of sample water.

Effects of pH

In the extraction of cobalt diethyldithiocarbamate and the washing to remove diverse radioactive metals, the effects of the pH of the aqueous phases were examined by the radiochemical technique with cobalt-60 tracer solution.

The range of pH for quantitative extraction of cobalt was 4·8–8·0, as shown in Fig. 1. This range is somewhat different from the value 4–11 quoted[2] for the extraction with carbon tetrachloride. The mid-range (pH 5–5·5) was chosen for use. The cobalt diethyldithiocarbamate, extracted into benzene, is very stable and is not affected by washing even with mercuric chloride solution at pH 2, as shown in Fig. 1. The pH of the washing solution used was adjusted to 3·5–4·0, but should be no higher than 5, since mercury(II) tends to hydrolyse.

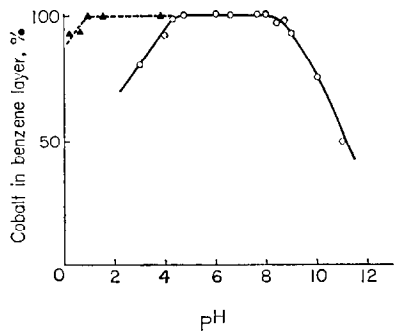

FIG. 1.—Effect of pH.
——○—— on the extraction of cobalt
- - -▲- - - of the washing solution on the extraction
Cobalt-60 tracer solution (54400 ± 150 cpm/ml) was used.

Amount of sodium diethyldithiocarbamate

Even when the extraction was made from 500 ml of sample water containing a few mg of diverse metal ions, 5 ml of 2% sodium diethyldithiocarbamate solution were sufficient for the quantitative extraction of cobalt. A large excess of the reagent did not affect the extraction. Since sodium diethyldithiocarbamate decomposes rapidly in acidic solution of pH below 6, the reagent solution should be added after the pH is adjusted to 5·0–5·5.

Volume of aqueous solution, addition of carrier, and time of shaking

The same results were obtained irrespective of the volume of aqueous phase, up to 500 ml. In the determination of trace amounts of radioactive cobalt (less than 10^{-9} g/ml), the addition of 25 μg of stable cobalt had no effect (Table I). Therefore, the addition of a carrier, used generally in the separation and determination of trace radioactive

TABLE I.—EFFECTS OF THE VOLUME OF SAMPLE SOLUTION AND ADDITION OF CARRIER

Volume of solution, *ml*	Non-active cobalt added, *μg*	Recovery of cobalt-60	
		cpm	%
50	0	54500, 52700, 53600, 54300	100, 97, 99, 100
	25	54300, 55400, 54000, 54300	100, 102, 100, 99
100	0	54800, 53300, 54500	101, 98, 100
	25	52600, 52800, 54900,	97, 97, 101
250	0	54000, 53300, 53900	100, 98, 99
	25	54500, 54300, 53300	100, 100, 98
500	0	53800, 53900, 54100	99, 99, 100
	25	54500, 54000, 54400	100, 100, 100

Each solution contained 54403 ± 233 gamma-cpm of the tracer, equivalent to 0·6 μg of cobalt.

nuclides, was not required. Moreover, in the presence of up to 5 mg of non-active cobalt, the recovery of trace amounts of cobalt-60 was not affected. Cobalt diethyldithiocarbamate was quantitatively extracted by vigorous shaking for 2 min. The concentration of the cobalt solution was without influence on the recovery (Table II).

TABLE II.—EFFECT OF THE CONCENTRATION OF COBALT

Volume of aqueous phase, *ml*	[Cobalt], *g/ml*	Recovery* of cobalt-60	
		cpm	%
100	$1{\cdot}87 \times 10^{-13}$	660, 640, 660	102, 100, 102
100	$9{\cdot}35 \times 10^{-13}$	3160, 3360, 3200	98, 103, 100
100	$1{\cdot}87 \times 10^{-12}$	6470, 6320, 6460	100, 98, 100
500	$3{\cdot}74 \times 10^{-14}$	650, 660, 660	101, 102, 102

* Cobalt-60 tracer solution containing 643 ± 12 gamma cpm/$1{\cdot}87 \times 10^{-11}$ g Co was used.

Washing solution

If the extract was washed with 20 ml of 0·05*M* mercury(II) chloride at pH 3·5–4·5, up to 5 mg of metals such as iron(III), nickel, manganese(II) and (III), and zinc were removed completely, while the trace amounts of cobalt-60 in the benzene remained there quantitatively.

Effects of foreign nuclides

The effects of various elements on the determination of cobalt were examined by the use of radioactive isotopes. Iron, copper, nickel, silver and zinc were extracted into benzene together with cobalt as the diethyldithiocarbamates. With the exception of palladium and platinum, the interferences of nuclides could be removed completely by washing the extract with mercury(II) chloride solution. Since mercury diethyldithiocarbamate is highly stable, the metals in other diethyldithiocarbamates are displaced by the mercury(II). The results obtained are shown in Table III.

TABLE III.—EFFECT OF FOREIGN NUCLIDES

Nuclides that do not form an extractable complex	Na-24, K-42, Cs-134m, Sr-89m, Ba-139, Sc-46, Zr-95, Hf-181, Sb-124, Ta-182, Ce-141, -144, Cl-38
Nuclides that form extractable complexes. These complexes are removed by washing	Ag-110m, Fe-59, Ni-65, Cu-64, Zn-65, Nb-95, Mo-99, Mn-54, Ga-72, In-114m, Tl-204, As-76, Sb-124, Bi-210, Se-75 (incompletely), Te-129
Nuclides that are not removed by washing	Pd-109, Pt-193, Se-75 (slightly)

In a reactor coolant water, the presence of palladium, platinum and mercury is rather unusual. If the coolant water contains such radioactive metals, they can be identified and their effects eliminated by gamma-ray spectrometry, because the gamma-ray energies and half-lives of these metals are different from those of cobalt-58 and -60.

Recovery and application

An average recovery of 99·5% was obtained from a cobalt-60 tracer solution. The relative standard deviation in the 25 determinations was 1·4%. The separation took 15 min.

Radioactive cobalt in the reactor coolant water of the Japan Power Demonstration

Reactor was determined by the procedure. A sample taken 13 hr after the initiation of the reactor operation at 16 MW contained long-lived nuclides such as manganese-54, chromium-51, iron-59 and zinc-65. A multichannel gamma spectrometer was used to identify the activities and to examine the purity of the separated fraction of cobalt-58 and -60.

The results obtained (cobalt-58 $1{\cdot}5 \times 10^{-2}$ μC/l and cobalt-60 $5{\cdot}0 \times 10^{-3}$ μC/l in the filtrate; cobalt-58 $2{\cdot}8 \times 10^{-3}$ μC/l and cobalt-60 $9{\cdot}0 \times 10^{-4}$ μC/l in the residue) agreed with those obtained by the standard method[1] and corresponded to less than 10^{-9} g of cobalt per ml.

Acknowledgement—The authors wish to thank Dr. T. Ishimori for useful comments on gamma spectrometry.

Zusammenfassung—Eine Trennung durch schnelle Extraktion zur radiochemischen Bestimmung von Kobalt-58 und Kobalt-60 in Reaktorkühlwasser wird beschrieben. Nach Einstellung des pH der Wasserprobe auf 5,0–5,5 wird Kobaltdiäthyldithiocarbamat mit Benzol extrahiert. Andere gewöhnlich im Reaktorkühlwasser vorhandene Nuklide wie Mangan-54 und -56, Kupfer-64 und Eisen-59 werden zusammen mit Kobalt extrahiert. Sie lassen sich jedoch leicht entfernen durch Waschen des Extrakts mit Quecksilber(II)chloridlösung. Die Kobalt-58- und -60-Aktivitäten werden durch Gammazählung eines Teiles vom gewaschenen Extrakt gemessen. Spuren von Radiokobalt in 500 ml Wasser konnen quantitativ ohne Träger extrahiert werden. Die Trennung ließ sich in 15 Minuten beenden, es wurde eine durchschnittliche Ausbeute von 99,5% mit einer relativen Standardabweichung von 1,4% in 25 Versuchen erzielt.

Résumé—On décrit une méthode de séparation rapide par extraction pour la détermination radiochimique du cobalt-58 et du cobalt-60 dans l'eau de réfrigération d'un réacteur. Après avoir ajusté le pH de l'échantillon d'eau à 5,0–5,5, on extrait le diéthyldithiocarbamate de cobalt au benzène. D'autres nucléides, par exemple manganèse-54 et -56, cuivre-64 et fer-59, qui sont habituellement présents dans l'eau de réfrigération du réacteur, sont également extraits en même temps que le cobalt. Toutefois, on peut aisément les éliminer par lavage de l'extrait avec une solution de chlorure de mercure (II). On mesure les activités des cobalt-58 et -60 par comptage gamma d'une partie aliquote de l'extrait lavé. On peut extraire quantitativement des traces de cobalt radioactif d'un échantillon d'eau de 500 ml sans emploi d'entraîneur. On peut achever la séparation en 15 mn, et l'on a obtenu une récupération moyenne de 99,5%, avec un écart type relatif de 1,4% (25 expériences).

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ION-EXCHANGE BEHAVIOUR OF SEVERAL ELEMENTS IN MIXED SOLVENTS

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Summary—The distribution coefficients between the cation- and anion-exchangers Dowex 50 and Dowex 1, and aqueous solutions containing nitric or hydrochloric acid and organic solvents with or without amines or complexing agents, have been obtained for a number of metals including uranium, thorium, cerium, iron, copper, and nickel. The organic solvents were methanol, acetone and dimethylformamide; the amines were tributylamine and tribenzylamine, and the complexing agents EDTA and citric acid. Both batch and column methods were used.

THOUGH data pertaining to the ion-exchange characteristics of various elements in mixed aqueous–organic solvents containing mineral acids are relatively numerous[1–3] no attempts have yet been made to investigate systems which also contain amines and/or organic complexing agents in addition to organic solvents and mineral acids. In order to obtain some information on the adsorption behaviour and separation possibilities of elements in the latter media, the research work presented in this paper was performed, with the widely used cation- and anion-exchange resins Dowex 50 and Dowex 1 in mixtures of three organic solvents with either hydrochloric or nitric acid, in the absence or presence of amines and/or organic complexing agents

EXPERIMENTAL

Reagents

Ion-exchange resins. The air-dried strongly acidic and basic, cation- and anion-exchangers, Dowex 50-X8 (100–200 mesh, hydrogen form) and Dowex 1-X8 (100–200 mesh: chloride or nitrate forms) were used for the batch and column experiments.

Standard solutions. Exactly weighed amounts of UO_2(II), Th, Ce(III), Fe(III), Co, Ni, Mg, Ca, Al, Cr(III), Cu(II), Mn(II), Mo(VI), Sr and Zr as chlorides or nitrates were dissolved in 6*M* or 12*M* hydrochloric or nitric acid to give concentrations of the ions of about 10 mg/ml.

Solvents. The reagent-grade organic solvents used were methanol, acetone and dimethylformamide (DMF).

Amines and complexing agents. These were tributylamine (TBA), tribenzylamine (TBeA), EDTA (disodium salt) and citric acid.

Determination of the various elements

Most of the elements investigated (in amounts exceeding *ca.* 100 μg) were determined titrimetrically with EDTA. Microgram quantities of the metal ions were determined spectrophotometrically,[4] or fluorometrically in the case of uranium.[5]

Determination of distribution coefficients

The weight distribution coefficients of the elements were determined by using either the batch equilibrium method (batch method) or the column method. Because details of these methods have already been reported[3] no further description will be given here.

RESULTS AND DISCUSSION

In Table I are shown the distribution coefficients of several elements on Dowex 50, measured in a medium consisting of 90% DMF and 10% 6*M* hydrochloric acid (v/v).

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TABLE I.—CATION-EXCHANGE DISTRIBUTION COEFFICIENTS OF VARIOUS METAL IONS IN 90% DMF–10% 6*M* HCl

Al(III)	Ca(II)	Ce(III)	Co(II)	Cr(III)
280	15	160	0·6	<1*
Fe(III)	Mg(II)	Mn(II)	Mo(VI)	Cu(II)
<1*	15*	2·2	<1*	<1*
Th(IV)	UO_2(II)	Zr(IV)	Ni(II)	Sr(II)
>10^3	<1*	18	4·6	39

* Column method; other results by batch method.

The distribution values with an asterisk were determined by the column method with 1 mg of the metal ion per gram of resin. The other values were determined by the batch method with a load of 50 mg of metal ion per gram of resin except for aluminium of which 10 mg were taken. From these results it is seen that all those metal ions that form relatively strong anionic chloro-complexes are virtually not retained by the resin, *i.e.*, they show distribution coefficients which are less than unity. An exception is chromium which is known to form no anionic complexes of this kind. The extraordinary behaviour of this element may, however, be attributed to its strong tendency to form complexes with DMF so that chromium is not retained by the cation-exchanger.

The effect of changing the concentrations of DMF and hydrochloric acid was investigated for several of the strongly adsorbed elements listed in Table I. The results are listed in Table II from which it is seen that in some cases the distribution coefficients of the elements decrease with an increase of the concentration of DMF. This is

TABLE II.—VARIATION OF CATION-EXCHANGE DISTRIBUTION COEFFICIENTS WITH CHANGING CONCENTRATIONS OF DMF AND HCl

Ion	Overall [HCl], *M*	DMF, %											
		95	90	80	70	60	50	40	30	20	10	5	0
Al(III)*	0·6	>10^3	280	114	320	131	400	>10^3	>10^3	>10^3	>10^3	—	214
	1·2	—	24	17	18	22	27	24	22	18	18	—	—
Ca(II)†	0·6	—	15	15	16	16	17	16	15	14	15	20	24
Ce(III)†	0·6	195	160	200	320	580	860	980	~10^3	>10^3	>10^3	—	—
	1·2	—	61	63	63	80	82	82	80	80	80	—	140
Th(IV)†	0·6	—	>10^3	at all concentrations									
Zr(IV)†	0·6	—	18	13	25	54	54	91	270	>10^3	>10^4	—	—

* 10 mg of ion per gram of resin, batch method.
† 50 mg of ion per gram of resin, batch method.

especially notable in the case of cerium and zirconium at 0·6*M* overall hydrochloric acid concentration. This effect is probably due to increased anionic complex formation in the DMF phase with increasing concentration of this solvent. Irregular variations which cannot be accounted for are also observed with other elements, *e.g.*, aluminium.

In Table III is shown the effect of changing concentrations of DMF, acetone and hydrochloric acid on the distribution coefficients of cerium and thorium. At the concentrations of hydrochloric acid marked *a–g* the sum of the DMF and acetone concentrations are, respectively, 90, 80, 78, 74, 70, 88 and 68%. From the data shown in Table III it is seen that the distribution coefficient of cerium at overall acid concentrations from 1·2 to 3·6*M* decreases with an increase of the DMF concentration.

TABLE III.—VARIATION OF CATION-EXCHANGE DISTRIBUTION COEFFICIENTS OF Ce AND Th WITH CHANGING CONCENTRATIONS OF DMF, ACETONE AND HCl

Ion	Overall [HCl], *M*	DMF, %										
		95	90	80	70	60	50	40	30	20	10	0
Ce*	0·6	200	—	—	—	—	—	—	—	—	—	—
	1·2[a]	—	53	62	70	170	230	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
	2·4[b]	—	—	20	27	45	85	185	$>10^3$	$>10^3$	$>10^3$	$>10^3$
	2·6[c]	—	—	21	29	36	—	—	—	—	—	—
	3·1[d]	—	—	13	17	31	37	146	470	$>10^3$	$>10^3$	$>10^3$
	3·6[e]	—	—	—	17	24	52	110	370	$>10^3$	$>10^3$	$>10^3$
Th†	0·6[a]	—	$>10^3$	at all concentrations								
	1·3[f]	—	$>10^3$	at all concentrations								
	2·5[c]	—	—	32	$>10^3$	at all other concentrations						
	3·0[d]	—	—	24	—	54	117	210	$>10^3$	—	—	$>10^3$
	3·7[g]	—	—	—	33	53	83	122	—	—	—	$>10^3$

* 8 mg Ce per gram resin, batch method.
† 10 mg Th per gram resin, batch method.

This is in accordance with the data presented in Table II and may be attributed to increased anionic complex formation with an increase in the concentration of the organic solvents. In the case of thorium this decrease of adsorption can be observed only at high concentrations of hydrochloric acid and organic solvents.

In Table IV are listed several solvent systems in which the distribution coefficients of iron, nickel and copper have been measured on Dowex 50. All of the distribution

TABLE IV.—CATION-EXCHANGE DISTRIBUTION COEFFICIENTS OF Fe(III), Ni(II) AND Cu(II) IN VARIOUS SOLVENT SYSTEMS

Solvent system composition	Fe	Ni	Cu
90% Methanol 0·6*M* in HCl and 0·1*M* in TBeA	1	$>10^2$	6
90% Methanol 0·6*M* in HCl	5	$>10^2$	8
90% Methanol 0·6*M* in HCl and 0·02*M* in EDTA	4	30	1
90% DMF 0·6*M* in HNO_3	100	65	8
90% Methanol 0·6*M* in HNO_3 and 0·01*M* in EDTA	>500	150	110
90% Methanol 0·6*M* in HNO_3	>500	400	250
90% Acetone 0·6*M* in HNO_3	>500	>500	>500
75% Acetone 0·6*M* in HNO_3	>500	>500	>500
90% Acetone 0·6*M* in HNO_3 and 0·5*M* in citric acid	>500	>500	>500
90% Acetone 0·6*M* in HNO_3 and 1·25*M* in citric acid	>500	>500	>500
75% Acetone 0·6*M* in HNO_3 and 0·025*M* in EDTA	21	21	21
72% Acetone 1·2*M* in HNO_3 and 0·04*M* in EDTA	17	25	9
72% Acetone 1·2*M* in HNO_3	>500	400	>500

values were determined by the column method with 1 mg of metal ion per gram of the resin. From these distribution data it is evident that in the hydrochloric acid media the distribution coefficients of nickel are invariably higher than those of the other two elements. This is due to the fact that iron and copper form anionic complexes which prevent the adsorption of these two elements on the resin. In the medium that is 0·1*M* in TBeA the distribution coefficients of iron and copper are lower than they are if the TBeA is omitted. This is very probably due to the CIESE-effect observed earlier.[6] A similar observation, although much less pronounced in the case of iron adsorption, was made for the hydrochloric acid system containing EDTA. Because

the distribution coefficient of nickel in this system also has a much lower value, the decrease in the distribution coefficients can very probably be attributed to the formation of EDTA-complexes which reduce the adsorbability of these elements on the resin. This effect of EDTA is rather small, however, because of the relatively high acidities involved.

In the methanol and acetone systems containing nitric acid alone or with EDTA or citric acid, the values of the distribution coefficients of iron, copper and nickel are generally much the same as each other (see Table IV). The coefficient for copper is, however, in several cases lower than that of the other two elements. This may be due to anionic nitrate complex formation. A similar observation has been made earlier[3] in studies involving the change of its distribution value on the same resin with variation of the nitric acid concentration.

Batch-method investigations of the anion-exchange behaviour of several metal ions in a mixture consisting of 90% DMF and 10% 6*M* hydrochloric acid (v/v) showed that in this medium the distribution coefficients of aluminium, cerium(III), cobalt, copper(II), iron(III), manganese(II), nickel, and thorium have values of <1, <1, 29, 29, <1, 18, <1, and <1 respectively. In the case of aluminium the loading was 10 mg/g of Dowex 1. All other loadings were 50 mg/g. These results show that the elements which are not adsorbed on strongly basic resins from any concentration of pure aqueous hydrochloric acid solutions (Al, Ce, Ni and Th) are also not retained on Dowex 1 from the DMF medium. On the other hand iron(III), which is strongly retained from pure aqueous hydrochloric acid solutions, is also not adsorbed from this organic solvent medium. This is very probably due to the influence of DMF which like acetone or tetrahydrofuran causes the CIESE-principle[6] to become effective.

It was also found that the distribution values of aluminium, cerium and thorium on Dowex 1 did not change when the DMF and hydrochloric acid concentrations were varied from 0 to 90% and 0·6 to 1·2*M* respectively.

In hydrochloric acid media containing both DMF and acetone, with the compositions listed in Table III, cerium and thorium were also not retained on Dowex 1 except at low concentrations of DMF (0 to 10%), for which the distribution coefficients were of the order of <100.

In Table V are shown the distribution coefficients of iron, nickel and copper on Dowex 1 for media of various compositions.

From the acetone–hydrochloric acid media in the presence or absence of TBA, iron is not retained by Dowex 1 owing to the CIESE-effect caused by the presence of acetone.[6] On the other hand from the methanol–hydrochloric acid media (see Table V) the adsorption of iron is high but decreases with increasing concentration of tertiary amine so that in this case the CIESE-effect is due to the presence of these amines. The CIESE-effect is not active in pure methanol–hydrochloric acid systems.[6]

In the nitric acid media only relatively small variations in the distribution coefficients of iron, nickel and copper are observed (see Table V). All of the distribution values listed in Table V were determined by the column method using 1 mg of metal ion per gram of Dowex 1.

By the use of one or the other of the media shown in Tables I–V several possibilities exist for analytical separations of the elements. Thus in 90% DMF–10% 6*M* hydrochloric acid, iron together with other elements can be separated on Dowex 50 from

TABLE V.—ANION-EXCHANGE DISTRIBUTION COEFFICIENTS OF Fe(III), Ni(II) AND Cu(II) IN VARIOUS SOLVENT SYSTEMS

Solvent system composition	Fe	Ni	Cu
90% Acetone 0·6*M* in HCl and 0·1*M* in TBA	<1	21	50
90% Acetone 0·6*M* in HCl	<1	21	50
90% Methanol 0·6*M* in HCl and 0·1*M* in TBA	>300	1	>300
90% Methanol 0·6*M* in HCl and 0·5*M* in TBA	80	—	150
90% Methanol 0·6*M* in HCl	300	1	400
90% Methanol 1·2*N* in HCl and 1*M* in TBA	35	—	—
90% Methanol 0·6*M* in HCl and 0·1*M* in TBeA	>300	1	>300
90% Methanol 0·6*M* in HCl and 0·25*M* in TBeA	100	1	150
90% Methanol 0·6*M* in HCl and 0·02*M* in EDTA	>200	1	60
90% Methanol 0·6*M* in HNO_3 and 0·01*M* in EDTA	<1	1	1
90% Methanol 0·6*M* in HNO_3	1	1	1
90% Acetone 0·6*M* in HNO_3	9	8	11
90% Acetone 0·6*M* in HNO_3 and 0·5*M* in citric acid	1	1	4
90% Acetone 0·6*M* in HNO_3 and 1·25*M* in citric acid	<1	<1	—
75% Acetone 0·6*M* in HNO_3 and 0·025*M* in EDTA	3	1	1
75% Acetone 0·6*M* in HNO_3	<1	1	1
72% Acetone 1·2*M* in HNO_3 and 0·04*M* in EDTA	1	1	1
72% Acetone 1·2*M* in HNO_3	1	1	2

the alkaline earth metals, cerium, *etc.* (see Table I). Another example for a separation possibility is that of iron from nickel and copper on Dowex 1 with 90% acetone that is 0·6*M* in hydrochloric acid.

Zusammenfassung—Die Verteilungskoeffizienten zwischen den Kation- und Anionenaustauschern Dowex 50 und Dowex 1 und wäßrigen Lösungen, die Salpeter- oder Salzsäure enthalten, sowie organischen Lösungsmitteln mit oder ohne Amine oder Komplexbildner wurden für eine Anzahl Metalle bestimmt, darunter Uran, Thorium, Cer, Eisen, Kupfer und Nickel. Die organischen Lösungsmittel waren Methanol, Aceton und Dimethylformamid; die Amine waren Tributylamin und Tribenzylamin und die Komplexbildner EDTA und Zitronensäure. Die Austauscher wurden sowohl portionsweise als auch in Säulen verwendet.

Résumé—On a obtenu les coefficients de partage entre les échangeurs cationique et anionique Dowex 50 et Dowex 1, et des solutions aqueuses contenant les acides nitrique ou chlorhydrique et des solvants organiques avec ou sans amines ou agents complexants, pour un certain nombre de métaux comprenant l'uranium, le thorium, le cérium, le fer, le cuivre et le nickel. Les solvants organiques sont le méthanol, l'acétone et le diméthylformamide; les amines sont la tributylamine et la tribenzylamine, et les agents complexants l'EDTA et l'acide citrique. Les méthodes discontinue et sur colonne ont toutes deux été utilisées.

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SHORT COMMUNICATION

A novel multi-column gas chromatographic system

(*Received* 27 *April* 1967. *Accepted* 15 *May* 1967)

IN THE course of an investigation into the mechanism of the pyrolysis of propylene it was necessary to analyse quantitatively mixtures of some 25 products, each present in the sample at below the 0·1 μmole level. The products ranged from hydrogen to toluene and included a number of linear and cyclic olefins and dienes. The analysis of such complex mixtures presents two main difficulties. First, with any given column, co-elution of two or more components is a commonplace event. Secondly, the boiling point range is frequently so wide that complete analysis in one operation is lengthy and, additionally, leads to very low sensitivities for the high boiling components. In principle, the first of these difficulties might be overcome by using a capillary column of sufficient length but the sensitivity of such an arrangement would be very low. The alternative approach of temperature programming would overcome problems of sensitivity but would not, because of thermal inertia effects, allow the speed of analysis which is essential for our kinetic investigations.

These problems can, however, readily be solved by means of a suitable multi-column arrangement. The various possible systems have been discussed at length elsewhere.[1] In the present instance the simplest approach, in which all columns are operated individually but in parallel with a single injector, was found to be adequate. With this arrangement only one detector need be employed, but in the present work the nature of the sample made it necessary to use two, and these were connected in series (see Fig. 1). Thus, the column effluent, in nitrogen carrier gas, passed first to a katharometer where hydrogen was determined. Thereafter, the emergent gas stream joined a controlled flow of hydrogen, and the mixed gases passed to a flame ionization detector, where all other materials were determined.

The hub of the multi-column system is a novel rotary column-selector valve operating on the sloping O-ring principle first utilized in gas chromatography by Pratt and Purnell.[2] This valve consists of two identical sloping O-ring valves ganged to operate on a common axis. Each half-valve, and hence the valve as a whole, has four positions, one per column. In each of these positions the selector valve connects the inlet and the outlet of a single column to the injection line and to the detector respectively. Thus, four samples can be analysed in sequence on the four columns by operating the sampling valve in each of the four positions of the column-selector valve.

Figure 2 shows the selector valve with the key in position for operating a column connected across ports 1*a* and 2*a*. In this position the sample enters port 1, passes through the 0·003-in. space between key and barrel, leaves the valve at port 1*a* and enters the column. On leaving the column it follows a similar path in the other half of the valve, entering at port 2*a* and passing on the detector through port 2.

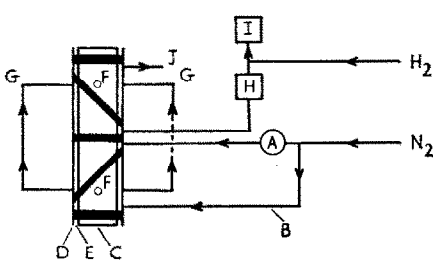

FIG. 1.—Flow diagram
(A) sampling valve; (B) flushing gas stream; (C) key of, and (D) barrel of column-selector valve; (E) clearance of 0·003 in, between key and barrel; (F) ports for connection to columns; (G) connected columns; (H) katharometer; (I) hydrogen flame ionization detector; (J) vent to atmosphere.

The *modus operandi* is the same for all other positions since the placing of ports 1 and 2 is arranged so that, independent of the orientation of the key, they always communicate with the appropriate annular space enclosed by the central and sloping O-rings. Similarly, ports 3 and 4 always communicate with the annular space enclosed by the *terminal* and sloping O-rings. Furthermore, the inlets of the three columns not in use, and also the outlets, are in communication *via* the terminal annular spaces, so that

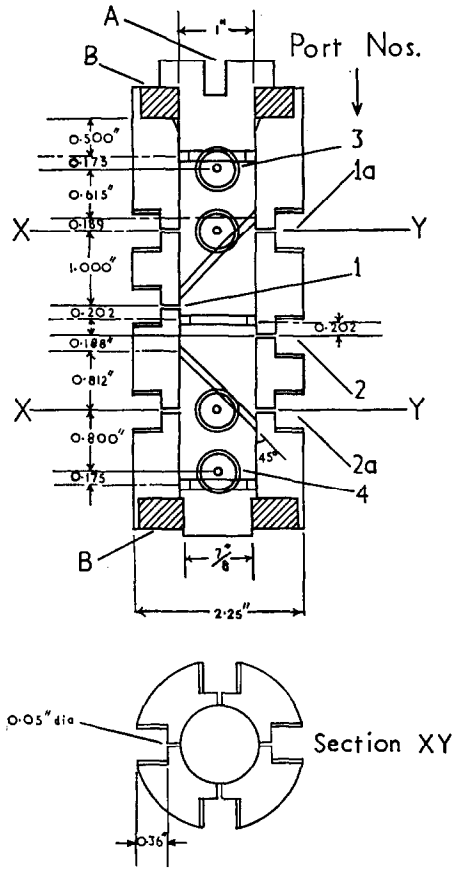

FIG. 2.—Longitudinal (top) and cross-sectional drawings of column-selector valve. Ports 3 and 4 have been projected down on to the plane of the longitudinal section: (A) slot for handle; (B) ball-race. The ports for connection to the four columns appear in the sections XY.

NOTES ON CONSTRUCTION

(1) The barrel was drilled for a diameter of 1 in. and the key was then machined to clear the barrel by 0·003 in.

(2) The dimensions of the grooves in the key are as follows;

sloping grooves: width = 0·125 in.; depth = 0·105 in.
straight grooves: width = 0·150 in.; depth = 0·115 in.

These grooves were designed to take neoprene O-rings with an internal diameter of 0·734 in. and a cross-sectional diameter of 0·139 in. (James Walker Ltd., Woking, England: PB 80/OS 15).

(3) The ports were drilled and tapped to take a ¼-in. B.S.P. fitting, but any convenient connection could be made. Great care was taken in deburring the 0·05-in. diameter holes (see Section XY) where they emerged into the barrel.

TABLE I.—DETAILS OF CHROMATOGRAPHIC COLUMNS

Column No.	Length, *cm*	Solvent	Solid support	Solvent–support ratio, % *w/w*
1	85	silicone oil	120/140 ASTM alumina	2·9
2	340	β,β'-oxydipropionitrile	100/120 ASTM sil-o-cel	15
3	150	squalane	120/140 ASTM sil-o-cel	25
4	75	squalane	120/140 ASTM sil-o-cel	6

these three columns are connected in parallel across ports 3 and 4 thereby enabling these ports to be used as entry and exit for a flushing gas stream.

Figure 1 illustrates a flow chart of the whole system. Since all columns are, in effect, in parallel and operate from a single back-pressure, the flow-rate through any given column is the same whether it is in use or not. This arrangement minimizes disturbances to the system caused by changing columns. Hence, after switching of columns the katharometer baseline rapidly took up a steady position while simple experiments with a soap bubble flow-meter showed that a stable flow-rate was attained almost immediately. Column switching could, therefore, be achieved in a matter of seconds merely by rotating the key of the valve through 90°.

The provision of flushing has the useful advantage that if the particular column in use is designed to deal with low boiling eluates there is no need to wait for the higher boiling point materials to be eluted before switching over to another column.

The use of several columns with different liquid phases is already a well-known and much-practised procedure for coping with multi-component peaks and no further elaboration of this theme will be undertaken here. The use of several columns with the *same* liquid phase is, however, not generally practised but it is clearly an approach which can be used to cope with mixtures which exhibit a wide range of boiling points, the objective being to adjust the length and solvent–support ratio of each column to deal with a given boiling point range. This expedient provides for faster and more

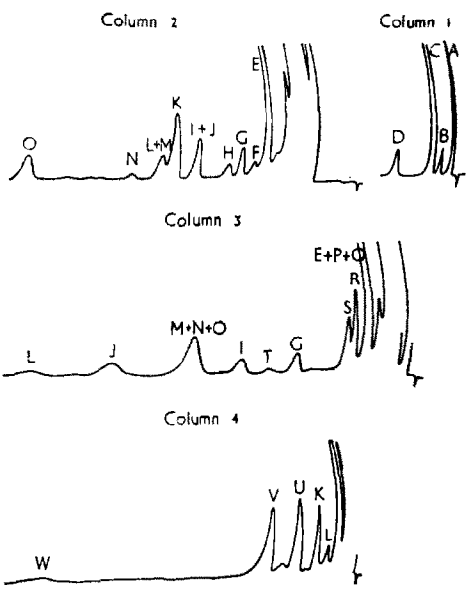

FIG. 3.—Sample chromatograms.
(A) methane; (B) ethane; (C) ethylene; (D) propane; (E) 1,3-butadiene; (F) *cis*-2-pentene; (G) 1,4-pentadiene; (H) 1-hexene; (I) isoprene; (J) cyclopentene; (K) 3-methylcyclopentene; (L) diallyl; (M) *trans*-1,3-pentadiene; (N) *cis*-1,3-pentadiene; (O) cyclopentadiene; (P) isobutene; (Q) 1-butene; (R) *trans*-2-butene; (S) *cis*-2-butene; (T) 1-pentene; (U) unidentified; (V) benzene; (W) toluene.

sensitive chromatography by reducing the retention volumes of the higher boiling materials. The columns used in this work, details of which are shown in Table I, were designed on this basis.

Analysis of the products of reaction from propylene pyrolysis was achieved as follows (see Fig. 3). First, hydrogen and the lower hydrocarbons up to propane were determined on column 1, the columns being switched before the emergence of the very large propylene peak. Then followed the elution on column 2 of a variety of hydrocarbons from 1,3-butadiene through 3-methylcyclopentene to 1,3-cyclopentadiene after which column 3 was engaged. This column was used to analyse cyclopentene and isoprene, and diallyl and *trans*-1,3-pentadiene, pairs of products which were simultaneously eluted on column 2. Finally, column 4, a shorter version of column 3, was used to analyse the higher products such as benzene and toluene.

This arrangement was found to be highly satisfactory for analysis of the products of propylene pyrolysis. However, with other mixtures it might be more convenient to utilize the presently described arrangement in other ways whilst still maintaining the economy of a single detector read-out system. For example, the use of phased injections may be advantageous for relatively simple mixtures. Then, by suitable adjustment of the phasing, the combined effluent from all columns would enable a chromatogram to be obtained in which all components are resolved at least once. The appearance of certain components more than once might be expected, and indeed this situation can be used as means of obtaining a double check of the determination of these components.

To take a different hypothetical example we may suppose that columns 1, 2 and 3 entail 5-min analyses and that the first eluate to be determined on column 4 does not emerge until 20 min after injection. Under these circumstances the present system can be used to inject a sample onto column 4 and then to conduct analyses, in turn, on columns 1, 2 and 3. Column 4 is then re-engaged and the total analysis completed. By this means the analysis time is virtually halved.

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Summary—Constructional and operating details are given of a special valve permitting selection of any one of four columns for connection to the detection system of a gas chromatograph, all four columns being connected to the carrier gas stream. If the retention times permit it, the columns may be used simultaneously for chromatographic separations and switched in turn into series with the detector for determination of the eluted components.

Zusammenfassung—Konstruktions- und Bedienungseinzelheiten eines Spezialventils werden angegeben, das die Auswahl einer von vier Säulen zur Verbindung mit dem Detektorsystem eines Gaschromatographen gestattet, wobei alle vier Säulen an den Trägergasstrom angeschlossen sind. Wenn es die Rententionszeiten erlauben, können die Säulen gleichzeitig zu chromatographischen Trennungen verwendet und nacheinander vor den Detektor geschaltet werden, um die eluierten Komponenten zu bestimmen.

Résumé—On donne des détails sur la construction et la manipulation d'une valve spéciale permettant la sélection de n'importe laquelle parmi quatre colonnes, afin de la relier au système de détection d'un chromatographe en phase vapeur, les quatre colonnes étant toutes reliées au courant de gaz porteur. Si les temps de rétention le permettent, on peut utiliser les colonnes simultanément pour les séparations chromatographiques et les relier successivement en série avec le détecteur pour la détermination des composants élués.

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PRELIMINARY COMMUNICATION

Fluorescent aluminium indicators derived from substituted coumarins

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DYES that function as metalfluorechromic indicators, containing the *o,o'*-dihydroxyazo group, have been prepared by coupling the diazonium salt of 1-amino-2-naphthol-4-sulphonic acid with the following fluorescent compounds: umbelliferone, 4-methylumbelliferone, 7-hydroxy-4-phenylcoumarin and 7-hydroxy-4-(4-methoxyphenyl)coumarin. The reaction was carried out under red light in a dark-room, at about 0°. The coumarin derivatives were dissolved in sodium hydroxide solution at pH 10, and a dilute solution of the diazonium hydrochloride was added slowly, the pH not being allowed to fall below 10 until the reaction was complete as shown by the Lindstrom and Diehl test.[1] From the products it was possible to isolate compounds which, though themselves non-fluorescent, gave an intense pink fluorescence with aluminium. The fluorescence developed slowly at room temperature but rapidly at 50–60°.

The fraction that was reactive towards aluminium was separated by ascending paper chromatography at 0° for 12 hr on Whatman No. 1 paper with ethanol–butanol–water–ammonia–0·2*M* EDTA (16:4:2:1:1) as solvent. These fractions all gave blue stains, the R_f values being 0·20 (umbelliferone derivative), 0·27 (4-methylumbelliferone), 0·38 (7-hydroxy-4-phenylcoumarin), 0·24 [7-hydroxy-4-(4-methoxyphenyl)coumarin]. On electrophoresis on Whatman No. 3MM paper, with a borax buffer at pH 9·8, at a potential of 180–220 V and current of 9–10 mA, the reactive species moved 1–2 mm in 90 min and were well separated from the other fractions obtained in the syntheses.

The reactive fractions were separated on the preparative scale by partition chromatography on a 40 × 5 cm column containing 150 g of standard grade Whatman Cellulose Powder or Whatman CF 11 Fibrous Cellulose Powder slurried in 600 ml of the solvent mixture used for the paper chromatography. The separations were made at about 0° in a refrigerated dark-room. The fractions obtained were dialysed to remove electrolytes, and the products were dried by freeze-drying.

The 4-methylumbelliferone derivative has been studied the most extensively. When 3–5 drops of a 1% solution of it in 50% aqueous ethanol are added to 2–100 μg of aluminium in 10 ml of solution at pH 4–5, a red-pink fluorescence is observed when the solution is exposed to ultraviolet light. The excitation spectrum has a maximum at 540 mμ and the emission spectrum has a maximum at 590 mμ. Under the conditions specified, Be, Mg, Zn, Cu, Fe, Co, Ni, UO_2, Ce, Cr, Na, K, Ca and Li ions do not give a fluorescence. At pH 3, In and Tl give a weak fluorescence. At the excitation maximum (440 mμ), 4-methylumbelliferone is not excited, so the products need not be purified before use in this reaction.

At pH 10 the dye has a violet-blue colour which changes to red-pink when a trace of metal ion is added. Calcium and magnesium form this red colour, which is reversibly discharged on addition of EDTA, suggesting that the compound may have an *o,o'*-dihydroxyazo structure.[2,3]

The purification and identification of these compounds are being studied, and methods developed for the determination of aluminium in biological materials.

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Summary—Metalfluorechromic indicators, containing the *o,o'*-dihydroxyazo group, have been prepared from a number of coumarin derivatives. The dye obtained from 4-methylumbelliferone reacts with 0·2–10 ppm of aluminium at pH 4–5 to give a pink fluorescence with an excitation peak at 540 mμ and an emission peak at 590 mμ.

Zusammenfassung—Aus einer Anzahl von Cumarinderivaten wurden die o,o'-Dihydroxyazogruppierung enthaltende Metall-Fluoreszenzindikatoren hergestellt. Der Farbstoff aus 4-Methylumbelliferon reagiert bei pH 4–5 mit 0,2–10 ppm Aluminium. Es resultiert eine rosa Fluoreszenz mit Anregungsmaximum bie 540 nm und Emissionsmaximum bei 590 nm.

Résumé—On a préparé des indicateurs métallofluorochromes contenant le groupe *o, o'*-dihydroxyazo à partir d'un certain nombre de dérivés de la coumarine. Le colorant obtenu à partir de la 4-méthylombelliférone réagit avec 0,2–10 p.p.m. d'aluminium à pH 4–5 en donnant une fluorescence rose avec un pic d'excitation à 540 mμ et un pic d'émission à 590 mμ.

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LETTER TO THE EDITOR

Identification of electrolysis products at the dropping mercury electrode by submicro-analysis and flame-ionization detection

SIR,

To elucidate the processes at the dropping mercury electrode it is essential to identify the electrolysis products and to determine, if possible, their yields. Generally, the mercury pool electrode has been used for this purpose. Although the products formed at the pool electrode and at the dropping electrode are often identical, exceptions have been reported recently;[1,2] hence it is always preferable to use a dropping mercury electrode for all preparative electrolyses aimed at elucidation of the electrode processes at it. To maintain a reasonable time-period it is then necessary to use small volumes (0·1–1·0 ml) of the solution for electrolysis. To exclude the effects of adsorption phenomena and of higher order reactions, it has proved in many instances preferable to keep the concentration of the electroactive substance below $2 \times 10^{-3}M$. Under such conditions the electrolysis product is obtained in about 0·5 ml of a millimolar solution, and it is impossible to use many of the isolation and identification techniques which are applied in preparative controlled potential electrolysis with a mercury pool electrode. Recently we have had some success in applying two techniques (in addition to ultraviolet spectroscopy and electrochemical techniques previously used for such purposes) namely submicro methods and gas–liquid chromatography with flame ionization detectors.

A 70% complete electrolysis of 1 ml of a $0{\cdot}001M$ solution of a compound with molecular weight about 100, yields about 70 μg of the electrolysis product. The solution can be analysed by conventional submicro procedures.[3] For example, in the one-electron electrolytic reduction of cinnamaldehyde in acid media it was possible to determine the pinacol yield by periodate oxidation[4] and the double-bond content by the bromine monochloride method.[5] The results enabled the dependence of the yields on electrolysis conditions[6] to be properly evaluated.

Although the dilution of the sample was too high to allow the application of conventional gas–liquid chromatography, flame-ionization detectors for gas–liquid chromatography have been successfully applied. When 0·5 ml of the electrolysed solution was extracted with 0·5 ml of ether, the volume reduced to 0·1 ml and a few microlitres injected on to a polyethylene glycol adipate column, good separation and peak shape were obtained for the electrolysis products of the two-electron reduction wave of cinnamaldehyde. Evaluation was carried out with a standard solution. Gas–liquid chromatography combined with mass spectrometry can be applied in a similar way. Further applications of these techniques are to be examined.

One of us (P. Z.) expresses his thanks to the Scientific Research Council and another (D. B.) to J. Lyons and Co. Ltd. for the grants that made this study possible.

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20 *June* 1967

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THE DETERMINATION OF TERVALENT CHROMIUM AND IRON IN CHROMIC ACID

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Summary—Chromic acid is analysed for tervalent chromium by separation of Cr(III) from Cr(VI) by precipitation as the hydrous oxide, with $Zn(OH)_3$ as a carrier. The hydrous oxide is collected by centrifugation and dissolved in perchloric acid, then Cr(III) is complexed with 1,2-diaminocyclohexanetetra-acetic acid and measured spectrophotometrically at 540 mμ. Repetitive analysis of a sample of chromic acid showed 93 ppm of Cr(III) ($s = 13$, $n = 9$). Iron in chromic acid is also separated as the hydrous oxide, then dissolved in HCl, reduced to Fe(II) with hydroxylamine hydrochloride, complexed with bathophenanthroline disulphonic acid and measured spectrophotometrically at 533 mμ. Repetitive analyses of a sample of chromic acid showed 2·6 ppm of iron ($s = 0{\cdot}35$, $n = 8$).

A NUMBER of papers have appeared describing the titrimetric determination of tervalent chromium in the presence or absence of sexivalent chromium by use of ethylenediaminetetra-acetic acid (EDTA).[1–4] Another paper describes the use, for spectrophotometric measurements, of the coloured species formed between chromium(III) and EDTA.[5] Titrimetric determination of chromium(III) with 1,2-diaminocyclohexanetetra-acetic acid (CDTA)[6] and its colorimetric determination with CDTA have also been described.[6,7]

Several techniques have been reported for the colorimetric determination of iron in the presence of chromium; these include use of 8-hydroxyquinoline,[8] 1,10-phenanthroline,[9,10] bathophenanthroline,[11,12] and thiocyanate.[13]

An EDTA titration was used in most of these methods in order to determine chromium(III) in the presence of chromium(VI). None of them was concerned with determination of micro quantities of chromium(III) and iron in "pure" chromic acid.

As a result of studies completed in our laboratory, new techniques were devised for the determination of these species in high-purity chromic acid.

EXPERIMENTAL

Reagents

All reagents were of highest purity. Distilled or demineralized water was used throughout.

Iron standard, 1 g/l. Iron wire was dissolved in hydrochloric acid and the solution diluted to volume. Appropriate dilutions were prepared as needed.

Chromium(III) solution, 1 g/l. Primary standard potassium dichromate (2·827 g) was reduced with hydrogen peroxide (acid solution), excess of hydrogen peroxide was removed by boiling, and the resultant solution was diluted to 1000 ml.

1,2-Diaminocyclohexanetetra-acetic acid (CDTA), 4% w/v. Sufficient sodium hydroxide was added to effect solution.

Bathophenanthroline disulphonic acid (disodium salt), 0·4% w/v aqueous solution.

Procedure for chromium(III)

Samples of chromic acid were dissolved in distilled water and transferred to a centrifuge tube, then 1 ml of 1% w/v zinc chloride solution was added followed by 6*M* sodium hydroxide added

dropwise until the colour of the solution changed from orange to yellow. The samples were centrifuged to collect the precipitate and the supernatant liquid was withdrawn by water-aspiration through a fine-tipped pipette. The hydrous oxides were washed twice with hot water (adjusted to pH 10 with sodium hydroxide) and centrifuged, and then the supernatant liquid was withdrawn as before. The hydrous oxides were then dissolved by adding 10% v/v perchloric acid, reprecipitated with sodium hydroxide, centrifuged, and the supernatant liquid was again withdrawn. Perchloric acid (10 ml, 10% v/v), was added, the centrifuge tube was heated, if necessary, to dissolve the hydrous oxides,

TABLE I.—EFFECT OF pH ON THE PRECIPITATION OF $Cr(OH)_3 . xH_2O$

pH	% Recovery of Cr(III)
9	101
10	100
11	100
12	103
13	87

TABLE II.—DETERMINATION OF 1·0 mg OF Cr(III) IN THE PRESENCE OF Na_2CrO_4

Na_2CrO_4 added, *mg*	Absorbance of Cr(III)–CDTA	
	Actual	Corrected*
0	0·208	0·208
10	0·245	0·208
20	0·286	0·206
50	0·390	0·205

* After subtracting absorbance of an equal quantity of Na_2CrO_4 solution carried through procedure, in the absence of added Cr(III).

TABLE III.—EFFECT OF IRON ON THE DETERMINATION OF Cr(III)

Cr(III) taken, *mg*	Fe, *mg*	Cr(III) found, *mg*	% Recovery
1	1	1·0	100
1	5	1·1	110
1	10	1·1	110

and 4 ml of CDTA were added. The pH was adjusted to 3·0 with 1*M* sodium hydroxide and the solutions were boiled for 20 min, cooled, transferred to 100-ml volumetric flasks, and diluted to volume. The absorbance of the solutions was read at 540 mμ, distilled water being used as reference. A standard calibration curve was prepared by placing various quantities of the chromium(III) solution in beakers, adjusting the pH, adding CDTA and completing as above. The effect of pH on the precipitation of hydrous chromic oxide in the absence of chromium(VI) was investigated with the chromium(III) standard (1 g/l) as the source of chromium. The results are shown in Table I.

To 10-ml aliquots of the chromium(III) standard solution (1 g/l) were added various amounts of reagent-grade sodium chromate solution (1 g/l) and then chromium(III) was determined as before. The results are shown in Table II.

The effect of iron on the determination of chromium(III) was investigated by mixing standard solutions of chromium(III) and iron and determining chromium(III) as before. The results are shown in Table III.

Repetitive analyses by this technique, completed by three analysts, of a sample of chromic acid showed it to contain 93 ppm of chromium(III) (9 variates, standard deviation 12 ppm).

Procedure for iron

Chromic acid solutions containing iron were treated as before, except that the precipitate was dissolved in 5 ml of dilute hydrochloric acid (1 + 4), 10 ml of absolute ethanol were added, and the solution was heated to reduce any chromium(VI) present. The solution was transferred to a 100-ml volumetric flask, 3 ml of 45% w/v sodium acetate trihydrate solution, 10 ml of 20% w/v hydroxylamine hydrochloride solution, another 5 ml of sodium acetate solution and 4 ml of bathophenanthroline disulphonic acid reagent were added. The solutions were diluted to volume and allowed to stand for 15 min, and the absorbance was measured at 533 mμ against a distilled water blank carried through the entire procedure. A standard calibration curve was prepared by placing various quantities of a diluted iron standard in 100-ml volumetric flasks, adding 5 ml of hydrochloric acid (1 + 4) and completing as above. The effect of chromium(III) on the iron determination was investigated by mixing standard solutions of each cation. The results are shown in Table IV.

The method of standard addition of iron to a chromic acid solution was used to test the accuracy of the iron determination. The results are shown in Table V.

Repetitive iron determinations on the sample of chromic acid used to establish the precision of the chromium(III) method showed 2·6 ppm of iron (8 variates, standard deviation 0·35 ppm).

TABLE IV.—EFFECT OF Cr(III) ON THE DETERMINATION OF 10 μg OF IRON

Cr(III) present, *mg*	Iron found, *μg*	
	Thioglycollic acid method	Bathophenanthroline disulphonic acid method
0·1	10·8	10·1
0·3	16·2	10·2
0·5	17·7	10·4

TABLE V.—RESULTS OF DETERMINATION OF IRON IN CHROMIC ACID FOLLOWING STANDARD ADDITIONS OF IRON

Iron present*, *μg*	Iron, *μg*		% Recovery
	Added	Found	
5·5	5·0	10·1	96
5·5	5·0	10·9	103
5·8	10·0	16·4	104
5·5	10·0	14·4	94
5·6	25·0	30·7	101
5·6	25·0	30·6	100

* As previously determined by the bathophenanthroline disulphonic acid procedure.

DISCUSSION

Studies showed that the chromium(III)–CDTA complex is equally well developed at pH 4·8 (recommended by Verma[7]) and pH 3·0; however, colour development is more rapid at pH 3·0. The boiling time was extended from 10 min (recommended by Verma) to 20 min because results obtained after boiling for only 10 min were erratic and did not conform to the Beer-Lambert law. Additional studies showed the colour of the chromium(III)–CDTA complex was stable for at least 60 hr when developed at pH 4·8. The colour developed at pH 3·0 reaches a maximum in less than 1 hr. The complex is formed more slowly at pH 4·8 and a 40-min heating time is necessary to ensure stable absorbances.

Although magnesium had been successfully used as a carrier for routine analyses of chromic acid for chromium(III) and iron, zinc was used when the effect of pH on the precipitation of chromium(III) was investigated (magnesium hydroxide is not significantly precipitated below pH 10). A further advantage was that zinc formed a less flocculent precipitate than magnesium did.

The study of the effect of pH on the precipitation of $Cr(OH)_3$ showed essentially no change in the range 9–12, but results were about 15% lower at pH 13. These results are not surprising, as chromium(III) is slightly amphoteric whereas zinc is very amphoteric. Thus, at pH 13, a large portion of the $Zn(OH)_2$ would dissolve, probably along with some of the $Cr(OH)_3$.

Although the chromium(III)–CDTA complex ion has an absorptivity only 1/10 to 1/100 that of many organometallic species used in spectrophotometry, its absorbance is linear over a wide concentration range (0·2–8 mg/100 ml). The relative insensitivity of the colorimetric determination of Cr(III)—a reproducibility of 0·005 absorbance units on the spectrophotometer is equivalent to 25 μg of chromium(III)—limits the expected accuracy of the procedure to 2·5% relative at the 1000-μg level. The relative precision of 4% commonly found for tervalent chromium(III) standards in the absence of chromium(VI) might reflect anomalies inherent in the precipitation and separation of chromium(III) as the hydrous oxide.

The extraction of the iron–bathophenanthroline complex (not the disulphonic acid) with chloroform yielded a linear calibration curve with standards (10–40 μg of iron), but the procedure gave erratic results when applied to samples of chromic acid. The reason for its failure is not clear since less chromium was present in this study than that reported in the literature.[12]

Iron values obtained by application of the thioglycollic acid procedure[16] tend to be higher than those found by use of bathophenanthroline disulphonic acid. Under the ammoniacal conditions used for completion of the thioglycollic acid method, a colloidal precipitate was formed. The nature of this precipitate was not established, but the higher iron result found was probably due to scattering of light by the precipitate.

Other techniques for the colorimetric determination of chromium(III) include use of Chromeazurol S[14] and diphenylcarbazide[15] [after separation of chromium(III) from chromium(VI)]; a titrimetric procedure using mercury(I) and permanganate is also reported.[17] Iron has been separated from chromium by extraction of iron(III) chloride into isopropyl ether,[18] by ion-exchange,[19,20] and with 8-hydroxyquinoline prior to an EDTA titration.[21] None of these procedures was evaluated in our studies.

Zusammenfassung—Chromsäure wird auf dreiwertiges Chrom analysiert, indem Cr(III) von Cr(VI) durch Fällung als Oxidhydrat mit $Zn(OH)_2$ als Träger abgetrennt wird. Das Oxidhydrat wird durch Zentrifugieren gesammelt, in Überchlorsäure gelöst, Chrom(III) mit 1,2-Diaminocyclohexantetraessigsäure in den Komplex überführt und bei 540 nm spektrophotometrisch gemessen. Wiederholte Analysen einer Probe von Chromsäure ergaben 93 ppm Cr(III) ($s = 13$, $n = 9$). Eisen in Chromsäure wird ebenfalls als Oxidhydrat abgetrennt, in HCl gelöst, mit Hydroxylaminhydrochlorid zu Eisen(II) reduziert, mit Bathophenanthrolindisulfonsäure komplex gebunden und spektrophotometrisch bei 533 nm gemessen. Mehrfachanalysen einer Chromsäureprobe ergaben 2,6 ppm Eisen ($s = 0{,}35$, $n = 8$).

Résumé—On analyse l'acide chromique pour le chrome trivalent par séparation de Cr(III) de Cr(VI) par précipitation à l'état d'oxyde hydraté, avec $Zn(OH)_2$ comme entraîneur. L'oxyde hydraté est recueilli par centrifugation et dissous en acide perchlorique, puis Cr (III) est complexé avec l'acide 1,2-diaminocyclohexanetétracétique et dosé spectrophotométriquement à 540 mμ. Des analyses répétées d'un échantillon d'acide chromique ont montré 93 p.p.m. de Cr(III) ($s = 13$, $n = 9$). Le fer dans l'acide chromique est aussi séparé à l'état d'oxyde hydraté, puis dissous en HCl, réduit en Fe(II) par le chlorhydrate d'hydroxylamine, compléxé avec l'acide bathoplénanthroline disulfonique et dosé spectrophotométriquement à 533 mμ. Des analyses répétées d'un échantillon d'acide chromique ont montré 2,6 p.p.m. de fer ($s = 0{,}35$, $n = 8$).

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MULTI-SPOT PAPER CHROMATOGRAMS OF SODIUM ORTHOPHOSPHATE

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Summary—The formation of two zones on paper chromatograms was investigated by chromatographing orthophosphoric acid and the primary, secondary and tertiary sodium salts, using pyridine–ethyl acetate/water as mobile phase. Movement of the species from the origin depends on washing the paper with acid and suggests an exchange of protons for sodium as a prerequisite condition. Washing with EDTA does not alter this requirement. Zone movement and multi-spot formation require that the forming solvent contain at least 5% of water (v/v). Between this value and saturation, increasing water content enhances zone disengagement. A solute spot of a sodium salt exchanges with the protons to produce a fast-migrating protonated phosphate species. If the solute sample has a sodium content less than the amount of exchangeable protons, a single fast spot is produced; if the concentration exceeds this capacity, a second slower spot results.

OCCASIONALLY, when a compound normally considered to be a single molecular species is chromatographed on paper, two or more distinct zones appear on the final chromatogram. The normal practice is to interpret this as an indication of two species. This exceptional behaviour has been termed multi-zoning or multi-spotting of a single species. Pollard *et al.*[1] summarized the origins of multi-spots as: (1) the alkaline-earth and heavy metal impurities in the paper;[2–4] (2) the water content of partially miscible solvent mixtures; (3) solute reaction with the mobile phase to form "solvated complexes"; (4) acidity; (5) anions which compete for the cation. The character of the multi-spot chromatogram depends upon the relative anion affinities for the cation and their concentrations. Specifically, Curry[5] investigated the chromatographic separation of phosphate species which are in equilibrium in aqueous solutions of sodium orthophosphates, *e.g.*,

$$H_2PO_4^- + B^{n-} = HPO_4^{2-} + HB^{(n-1)-} \quad (1)$$

where B^{n-} is some proton acceptor. He found that the number, position, and relative size of the spots, proposed to be $H_2PO_4^-$ and HPO_4^{2-}, were related to the concentrations of the different species in the sample solutions, these concentrations being determined by the solution acidity and the identity of the solute. Erdem[6] employed the suggestion to explain the identical phenomena for the sodium orthoarsenates. Pollard, Nickless, and Bigwood[7] observed multiple zones for orthophosphate in chromatographic systems employing anion-exchangers. Their zones were not as distinctly separated as those reported here, nor did these authors comment on the phenomenon or establish the identity of the species in these zones. Efforts to explain these observations generally propose the separation of species in equilibrium with

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each other [equation (1)]. Indeed Keller and Giddings[8] did conclude that multiple zones of a single solute on chromatograms can result from a slow transition between solute species. However, theory demonstrates that for multi-spotting by transition between species, the transition time, *i.e.*, the half-life, must be of the same magnitude as the time of formation of the chromatogram. The transition in equation (1) is a proton transfer and these tend to be very fast, *e.g.*, the half-life[9] for hydronium ion reacting with hydroxyl ion is about 10^{-8} sec. Equation (1) does not describe strictly the same situation, but other proton transfers would need to differ from this one by a factor of 10^{13} in order that the transition time and the period of chromatography be comparable. Thus the simple equilibrium of equation (1) seemed inadequate as an explanation because slow kinetic steps are required and are unlikely. The mechanism proposed here involves an ion-exchange process.

The first step in the problem was the verification that the separated spots obtained with phosphate salts are different phosphate species. Rommel and Keller[10,11] irradiated the completed chromatograms *in situ* with thermal neutrons to produce radioactive ^{24}Na and ^{32}P. Resolution of the activity *vs.* time curve of each zone gave the Na/P ratio. When double spots were produced with pyridine–ethyl acetate/water, the fast spot had Na/P ratios of 0·03–0·19 for the ortho-acid and any of its sodium salts, while the slow spot had Na/P = 0·75 for Na_2HPO_4 and 1·2 for Na_3PO_4. Similar phenomena were observed with a mobile phase of butanol/water, *e.g.*, with NaH_2PO_4, Na/P was 0·38 for the fast spot. Sodium was found in the fast zone for a sample of orthophosphoric acid.

EXPERIMENTAL

The glass chromatographic chamber for descending technique was that pictured by Macek.[12] The chromatograms were performed on 55 × 2·8 cm strips cut from sheets of Whatman No. 1 filter paper, acid washed. The start was always 8·6 cm from the end of the paper. Prior to chromatography the chamber was saturated with vapours of water containing the organic phase of the forming solvent. The sample was delivered to the dry paper by a 10-μl pipette to give a spot 1·5 cm in diameter, and the solvent was evaporated off. The sample-laden paper was placed in the vaporous atmosphere of the tank for at least 8 hr prior to chromatography. The sample solutions contained at least the minimum amount for detection by the colour reagent, *i.e.*, $10^{-3}M$ in phosphate. Completed chromatograms were air-dried and scanned for radioactivity, or the zones were revealed with the molybdate reagent.[13] Radiocounting procedures and equipment are described elsewhere.[11]

Pretreatment of the paper

Papers were washed and rinsed consecutively with (*a*) 2*M* acetic acid and 0·1*M* EDTA (*b*) 2*M* acetic acid, 0·1*M* EDTA and 2*M* acetic acid, (*c*) 2*M* acetic acid, (*d*) 2*M* hydrochloric acid, or (*e*) water. The acetic acid prewash was selected on the recommendation of Hanes and Isherwood[3] as sufficient to meet Pollard's first point. Each paper was immersed in the wash liquids for 5 min and rinsed by transfer through a series of immersions in distilled water until the acidity of the rinse remained that of distilled water. This rinse preceded the next wash solution. Finally the paper was rinsed with 20 ml of 95% ethanol (reported by Hettler[14] to prevent shrinkage of the paper) followed by 20 ml of ethyl acetate. The papers were dried in a fume-hood and stored. Storage did not change the chromatographic behaviour. Analyses by neutron activation[10,11] indicated that acid washing reduces the sodium content by a factor of 7 to 8. Some labile sodium still remains, however, since chromatography reduced the sodium content by a factor of 12 below that of the acid washed paper.

The solute for one set of these papers was 0·01*M* sodium dihydrogen phosphate and for the other 0·01*M* sodium dihydrogen phosphate plus 0·01*M* sodium acetate; both sets were formed with pyridine–ethyl acetate/water. Papers washed exclusively with water or not washed at all gave little or no movement of either solute solution; the spot "smeared out" from the origin. The sodium dihydrogen phosphate, when alone, gave a single spot of identical shape and R_f for all pre-washed papers. This salt combined with sodium acetate gave identical double spots, similar to those shown in Fig. 1, for all pre-washed papers. When only EDTA was used, *i.e.*, no acid wash, the phosphate

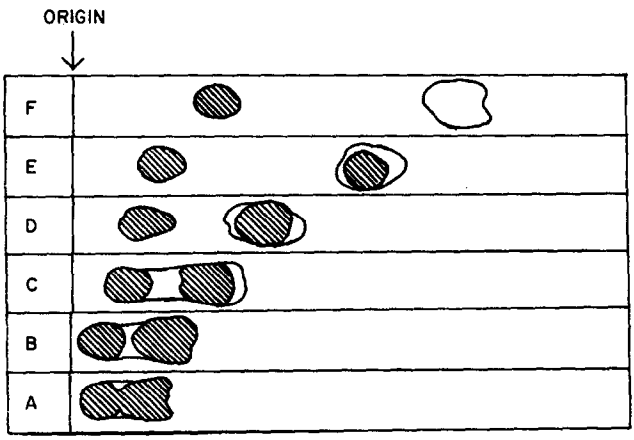

FIG. 1.—Formation of phosphate multi-spots from 0·01*M* sodium dihydrogen phosphate, 0·02*M* sodium acetate developed with pyridine–ethyl acetate/water. Hatched areas are regions of greatest colour intensity.

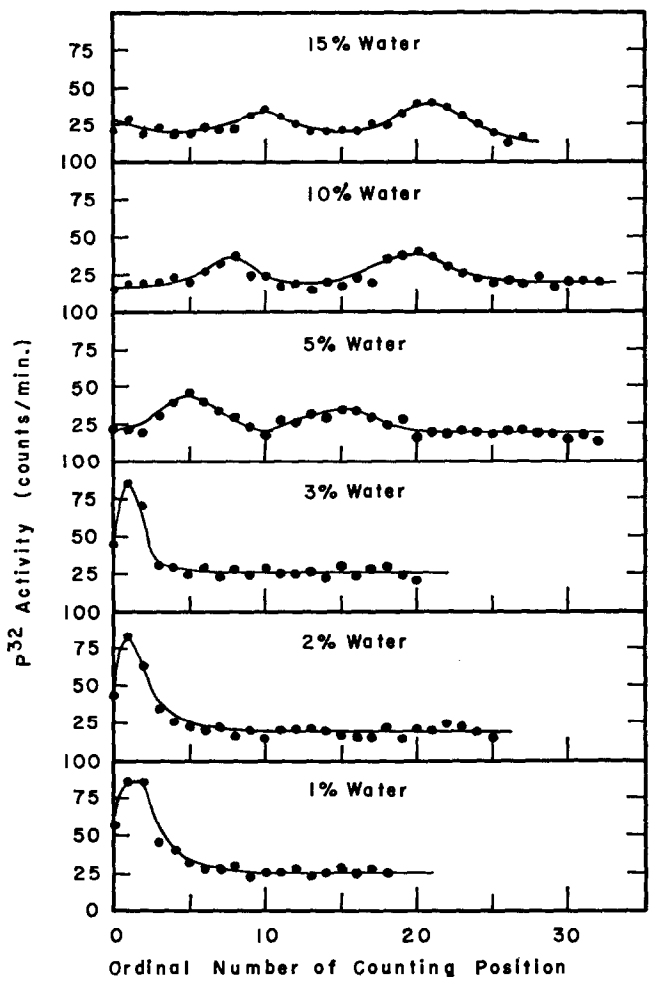

FIG. 2.—Concentration profiles of phosphate radiochromatograms formed with pyridine–ethyl acetate/water with varying amounts of water.

TABLE I.—EFFECT OF SOLUTE CONCENTRATION ON DOUBLE SPOT FORMATION

Solute	No.	[Solute], *M*	[Na^+], *M*	[Total phosphate species] *M*	Na/P	Result
H_3PO_4	1-1	0·01	0	0·01	0	1 spot
	1-2	0·05	0	0·05	0	1 spot
	1-3	0·10	0	0·10	0	1 spot
NaH_2PO_4	1-4	0·001	0·001	0·001	1	1 spot
	1-5	0·01	0·01	0·01	1	1 spot, $R_f = 0·64$
	1-6	0·02	0·02	0·02	1	2 spots
	1-7	0·05	0·05	0·05	1	2 spots
	1-8	0·10	0·10	0·10	1	2 spots
Na_2HPO_4	1-9	0·01	0·02	0·01	2	1 spot, $R_f = 0·64$
Na_3PO_4	1-10	0·01	0·03	0·01	3	2 spots, $R_f = \begin{cases} 0·64 \\ 0·40 \end{cases}$

remained at the origin with a forming solvent of butanol/water and gave an elongated smear with pyridine–ethyl acetate/water.

Papers washed with 2*M* acetic acid were used throughout the study of other variables.

Composition of the developer

The forming solvent routinely used was the 0·45:1 (v/v) pyridine–ethyl acetate combination, containing water.[8] Initial vagaries led to an investigation of the effect of water content of the forming solvent. The solvents used to prepare the mobile phase were analysed for water by titration with Karl Fischer reagent. Once the water content of the reagents was known, water could be added to produce a desired composition.

The solution chromatographed in these studies was one of radioactive 0·01*M* disodium hydrogen phosphate adjusted to pH 8·5 with dilute sodium hydroxide. The chromatograms were formed for identical time periods with pyridine–ethyl acetate mixtures of known but varying water content. Figure 2 is a plot of the radioactivity measured by the techniques described elsewhere.[11] With up to 5% of water in the mobile phase, there is only one zone, which essentially does not migrate. As the water content increases, more phosphate appears in a fast zone and there is increased separation of the zones. The saturation composition of 24% was determined by titration of the non-aqueous components to an opalescence with water. This water-saturated pyridine–ethyl acetate mixture gave only the fast spot. The 15% aqueous solution was used throughout the work unless otherwise noted.

Total solute concentration

Table I indicates the dependence of double zoning on the total solute concentration. The concentrations of sodium and *total* phosphate species, disregarding the particular ionic species involved, are shown along with the Na/P ratios. The R_f-values are reported where they were observed. In most cases, clear separations were produced only after mobile phase ran from the end of the paper. No attempt was made to control the acidity of the solution applied.

TABLE II.—EFFECT OF THE Na/P RATIO ON RELATIVE SPOT SIZE OF DOUBLE SPOTS FROM 0·01*M* TERTIARY SODIUM ORTHOPHOSPHATE

No.	Additive	[Na], *M*	[Total phosphate species] *M*	Na/P	Result
2-1		0·03	0·01	3	Two spots, slow spot ¼ the size of the fast spot
2-2	0·01*M* NaOH	0·04	0·01	4	Two spots, slow spot ½ the size of the fast spot
2-3	0·01*M* NaOAc	0·04	0·01	4	Two spots, slow spot ½ the size of the fast spot
2-4	0·01*M* NaOH + 0·01*M* NaOAc	0·05	0·01	5	Two spots of about equal size

Sodium to phosphorus ratio

Table II presents the results of the chromatography of 0·01*M* trisodium phosphate with the additives listed. Table III shows the results for various ratios and concentrations of sodium and phosphate for solutions prepared from sodium dihydrogen orthophosphate and sodium acetate.

TABLE III.—EFFECT OF THE SODIUM/PHOSPHORUS RATIO AND THE SALT CONCENTRATION ON THE APPEARANCE OF DOUBLE SPOTS

No.	[Total phosphate species], *M*	[Na], *M*	Na/P	Result
3-1	0·001	0·001	1	1 spot
3-2	0·01	0·01	1	1 spot
3-3	0·02	0·02	1	2 spots
3-4	0·05	0·05	1	2 spots
3-5	0·01	0·02	2	2 spots
3-6	0·01	0·04	4	2 spots

Effect of pH of the applied solution

The effect of pH of the sample solution on multi-zoning was investigated most extensively. Table IV shows the composition of the various solutions chromatographed, and the results. All the

TABLE IV.—CHROMATOGRAMS OF ORTHOPHOSPHATES AT VARIOUS pH VALUES OF THE SOLUTION APPLIED

Paper No.	Solution applied	pH	Description*	
Tertiary sodium orthophosphate				
4-1	0·01*M* Na_3PO_4	12·3	S	F
4-2	0·01*M* Na_3PO_4 + NH_3 + HCl	12·3	S	F
4-3	0·01*M* Na_3PO_4 + HCl	9·0	S	F
4-4	0·01*M* Na_3PO_4 + HCl	6·8	S	F
4-5	0·01*M* Na_3PO_4 + HCl	4·0	S	F
4-6	0·01*M* Na_3PO_4 + HCl	2·1	S	F
Secondary sodium orthophosphate				
4-7	0·01*M* Na_2HPO_4	7·5	S	F
4-8	0·01*M* Na_2HPO_4 + NH_3	12·0	S(t)	F
4-9	0·01*M* Na_2HPO_4 + NH_3 + HCl	9·0	—	F
4-10	0·01*M* Na_2HPO_4 + HCl	7·0	S(t)	F
4-11	0·01*M* Na_2HPO_4 + HCl	4·0	—	F
4-12	0·01*M* Na_2HPO_4 + HCl	2·0	—	F
Primary sodium orthophosphate				
4-13	0·01*M* NaH_2PO_4	4·5	—	F
4-14	0·01*M* NaH_2PO_4 + NH_3	12·0	—	F
4-15	0·01*M* NaH_2PO_4 + NH_3	9·2	—	F
4-16	0·01*M* NaH_2PO_4 + NH_3	7·0	—	F
4-17	0·01*M* NaH_2PO_4 + NH_3 + HCl	4·5	—	F
4-18	0·01*M* NaH_2PO_4 + HCl	2·0	—	F
Orthophosphoric acid				
4-19	0·01*M* H_3PO_4	2·2	—	F
4-20	0·01*M* H_3PO_4 + NH_3	12·0	—	F
4-21	0·01*M* H_3PO_4 + NH_3	9·4	—	F
4-22	0·01*M* H_3PO_4 + NH_3	7·2	—	F
4-23	0·01*M* H_3PO_4 + NH_3 + HCl	4·0	—	F
4-24	0·01*M* H_3PO_4 + NH_3 + HCl	2·2	—	F

* F—fast spot, *i.e.*, large R_f.
S—slow spot, *i.e.*, small R_f.
t—threshold, *i.e.*, barely discernible separation.

chromatograms for any one phosphate solute were executed simultaneously in the same chamber with identical forming solvents for the same period of time.

Addition of sample to the paper at the instant the solvent reached or had just passed the origin resulted in smeared zones from which it was impossible to conclude anything.

Pyrophosphate as solute

The possibility that one of the spots was a condensed phosphate formed during the experiments seemed extremely remote, *e.g.*, Steinman, Lemmon and Calvin[15] found that a solution of phosphoric acid would not yield pyrophosphoric acid in the absence of a catalyst. Nonetheless, 0·1*M* primary and 0·1*M* secondary sodium orthophosphates were chromatographed simultaneously with 0·01*M* sodium pyrophosphate ($Na_4P_2O_7$). With 26·4% pyridine, 58·6% ethyl acetate, 15% water (v/v) as mobile phase, both the disodium orthophosphate and the pyrophosphate gave double spots but the zone locations and intensities were dramatically different and it seemed clear that very different ionic species were involved. With 24·8% pyridine, 55·2% ethyl acetate, 20% water (v/v), these salts formed single spots only, again at different positions.

DISCUSSION

Multi-zoning of a single species due to reversible transition between equilibrium forms is only possible with relatively slow kinetics. Therefore the multi-spots which occur with protonated phosphate must have some other explanation.

Acid washing is necessary to produce migration of the phosphate, and single and double spots can still be produced after this wash, even though this wash should have removed the heavy metals deemed necessary for multi-zones. EDTA, an excellent chelating agent for alkaline earths,[16] when used alone in neutral water as a pre-wash, led to retention at the origin and smeared chromatograms, but no multi-spots. When it was followed by acid, multi-spots resulted. The key to multi-spotting does not seem to be the removal of alkaline earths, but this removal followed by an acid wash.

Table IV shows that trisodium orthophosphate forms double spots in a range of pH values from acidic to basic. Multiple spotting seems to be independent of total salt content (Nos. 4-1 and 4-2) at the same pH (NH_4Cl present) and is identical for the same Na/P ratio and phosphate salt concentration at different acidities. The situation with secondary sodium orthophosphate probably represents threshold conditions for double spot formation and the system is highly sensitive to even minor differences in the solution applied. Double spots occur in Nos. 4-7, 4-8 and 4-10. The situation for 4-7 is identical with that of the entry for secondary sodium orthophosphate in Table I (single spot). We have no explanation for this except these sensitive threshold conditions. It is instructive that the double spots of Nos. 4-8 and 4-10 are nearly identical even though 4-8 is basic relative to the pure salt (4-7) while 4-10 is acidic. Table II reports chromatograms with 0·01*M* sodium hydroxide (2-2) and 0·01*M* sodium acetate (2-3) which were virtually identical. (Note that the concentrations of sodium ion are identical.) The result for the mixture of sodium hydroxide and sodium acetate was twice that of either one alone. If the relative size of the spots had depended on the presence of the basic hydroxyl ion, cases 2-2 and 2-4 would have been similar. The chromatograms are identical for primary sodium orthophosphate and represent the extreme situation of single spots only. For us, these results are a convincing argument that the acidity of the solution *applied* has little or nothing to do with the phenomenon, *e.g.*, Nos. 4-6, 4-12 and 4-18 vary by 0·1 pH unit and yet pass from a single to a double spot. To fully complete the theme, phosphoric acid was used as the starting material with acid, base (ammonia), or both added to cover a pH range of 2·2 to 12·0.

We propose that an ion-exchange mechanism is responsible for multi-spots and

that these appear at a particular concentration of sodium ion in the solution applied. Neutron-activation studies indicate that sodium occupies some or all of the exchange sites, and is not exchanged for protons when the paper is washed with EDTA alone or water alone. The solute zone, potentially the slow spot, "smears out" from the origin or does not move at all. Once the paper is acid-washed, most of the sodium is replaced by protons. Sodium ions in the solution applied can replace these protons. So long as the sodium content does not exceed the proton concentration available from the paper, and the Na/P ratio of the solute spot remains less than unity, a single fast spot appears (Na/P 0·03–0·19 for pyridine–ethyl acetate/water; 0·38 for butanol/water). If, however, the sodium content of the solution applied exceeds the capacity of the paper so that the solute spot has a Na/P ratio greater than unity, two spots appear, the usual fast spot of composition stoichiometrically near H_3PO_4 and a slow one of composition nearly that of NaH_2PO_4. If one takes the exchange capacity of paper to be the 0·008 mequiv/g given by Ultee and Hartel[17] (see Rommel and Keller[11]) and assumes complete protonation by prewashing, then the amount of hydrogen ions available is $6{\cdot}6 \times 10^{-5}$ mequiv/cm^2. The 10-μl sample covers 1·8 cm^2. The concentration of sodium needed to just replace this amount of hydrogen and have no excess of sodium remaining in the solute spot is 0·012*M*. Tables I–IV show that this is exactly the threshold concentration above which multiple spotting occurs.

The amount of fast and slow species is determined by the sodium ion removed by the paper, not by the acidity of the solution applied. As the fast spot moves out from the origin it retains its integrity because it encounters protonated paper. Some sodium ion is encountered since proton exchange is not complete. As the slow spot moves on, it enters proton-rich paper and exchanges sodium for hydrogen, but since it does not move very far (Fig. 1) there is not much conversion. The formation of a protonated species may also be retarded by a relatively large number of sodium ions by some sort of competition, *e.g.*,

$$HPO_4^{2-} + Na^+{\cdot}H_2O = NaPO_4^{2-} + H_3O^+$$

or if not by compound formation, then at least by some kind of ion-pair association. Proton exchanges between phosphate species in solution are probably fast, so that a single solute zone, characteristic of the equilibrium mixture, results.[8] This is very likely the reason for the spot moving at all. Since the mechanism is a cation–proton exchange, one may well wonder why ammonium ion, added to adjust the pH, does not introduce vagaries. Bark, Graham, and McCormick have shown that ammonium ion does not exchange with cellulosic protons.[8]

The dependence of multi-spots on the water content of the developer may be because a proton acceptor, a Brønsted base, must be present before the sodium can displace the protons. Sjövall Haahti, and Nyström[19,20] remark that the chromatographic behaviour of the sodium or potassium salt of dehydroepiandrosterone sulphate on a polar gel is completely altered when the water content of the developer is 3% or greater. They take this as evidence of dissociation of the salt in the more aqueous developer.

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Zusammenfassung—Die Bildung zweier Zonen auf Papierchromatogrammen wurde durch Chromatographieren von Orthophosphorsäure und ihren primären, sekundären und tertiären Natriumsalzen mit Pyridin/Äthylacetat/Wasser als mobiler Phase untersucht. Die Fortbewegung der Spezies vom Anfangspunkt hängt vom Waschen des Papiers mit Säure ab und deutet auf einen Austausch von Protonen für Natrium als Vorbedingung hin. Waschen mit EDTA ändert daran nichts. Die Zonenfortbewegung und die Bildung mehrerer Flecken erfordern einen Volumenanteil von mindestens 5% Wasser in der Entwicklungsflüssigkeit. Zwischen diesem und dem Sättigungswert fördert zunehmender Wassergehalt die Trennung der Zonen voneinander. Ein Fleck von einem gelösten Natriumsalz tauscht mit den Protonen aus und bildet eine schnell wandernde protonierte Phosphatspezies. Hat die gelöste Probe einen Natriumgehalt, der geringer ist als die Menge an austauschbaren Protonen, so wird nur ein schnell wandernder Fleck gebildet; steigt die Konzentration über diesen Wert hinaus, so entsteht ein zweiter, langsamer wandernder Fleck.

Résumé—On a étudié la formation de deux zones sur chromatogrammes de papier en chromatographiant l'acide orthophosphorique et les sels de sodium primaire, secondaire et tertiaire, utilisant comme phase mobile le mélange pyridine-acétate d'éthyle-eau. Le mouvement des espèces à partir de l'origine dépend du lavage du papier à l'acide et suggère un échange du sodium par des protons comme condition préalable nécessaire. Le lavage à L'EDTA ne change pas cette condition. Le mouvement de zone et la formation de taches multiples nécessitent que le solvant contienne au moins 5% d'eau (v/v). Entre cette valeur et la saturation, l'augmentation de la teneur en eau accroît la séparation de zone. Une tache d'un soluté d'un sel de sodium donne lieu à échange avec les protons pour produire un phosphate protoné migrant rapidement. Si l'échantillon dissous a une teneur en sodium inférieure à la quantité de protons échangeables, il se produit une seule tache rapide; si la concentration excède cette capacité, une seconde tache plus lente en résulte.

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THE MASS SPECTROMETRY OF METAL CHELATES—II

OXINATES OF COMMON METALS

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Summary—The mass spectra of the oxinates of zinc, iron(III), manganese(II), nickel, cobalt, aluminium, copper and magnesium have been measured. Concentrations of several of these chelates have been related to the integrated ion currents recorded at a significant *m/e* value during evaporation of the sample in the source of an A.E.I. M.S.9 mass spectrometer. The structural significance of some of the mass spectra is discussed.

IN a previous paper[1] a method was described for the detection and estimation of amounts of nickel dimethylglyoximate down to 10^{-12} g. In this method, a small sample of the chelate was evaporated into the source of an A.E.I. M.S.9 mass spectrometer. The ion current at *m/e* 288 corresponding to the ion $C_8H_{14}N_4O_4{}^{58}Ni^+$ was recorded continuously during the evaporation of the sample. The integrated ion current was then shown to be proportional to the amount of metal chelate evaporated. It is the purpose of the present paper to extend this method to the oxinates of a number of metals in order to investigate the suitability of oxine as a ligand for this specific purpose. At the same time, it is possible to obtain structural information on these metal chelates from an examination of their mass spectra.

EXPERIMENTAL

Reagents

The oxinates of zinc, iron(III), manganese(II), nickel, cobalt, aluminium, copper and magnesium were prepared by the methods described in "Oxine and its Derivatives".[2] Stock solutions of copper, aluminium and zinc oxinates were prepared by dissolving 10 mg of the chelate in 100 ml of chloroform.

The complete mass spectra were recorded by evaporating small solid samples of the chelates in the source of the mass spectrometer.

The method described previously was used to record the ion currents at significant *m/e* values during evaporation of samples introduced (in the form of their solutions in chloroform or dioxan) into the probe with the aid of a Hamilton syringe.

All measurements were made with an A.E.I. M.S.9 mass spectrometer fitted with a direct evaporation probe.

RESULTS AND DISCUSSION

Copper oxinate

The mass spectrum of copper oxinate is illustrated in Fig. 1. The spectrum is in accord with a metal : ligand ratio of 1 : 2 and there is an intense mass peak at *m/e* = 351 corresponding to the molecular ion $C_{18}H_{12}N_2O_2{}^{63}Cu^+$. The current from this ion was recorded in further quantitative measurements because it was characteristic of the molecule.

* Part I—*Talanta*, 1967, **14**, 777.

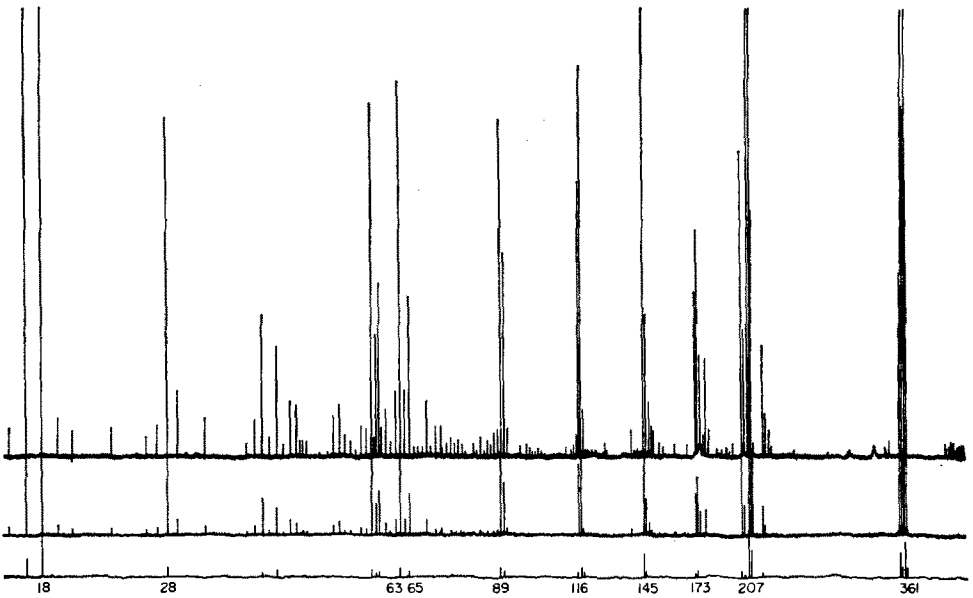

FIG. 1.—Mass spectrum of copper oxinate.

Using as reference peak the signal at *m/e* 219 obtained by admitting a measured pressure of heptacosafluoro tri-n-butylamine to the source, the integrated ion currents at *m/e* 351 were recorded when a range of measured samples of copper oxinate was evaporated into the ion source. The samples were introduced in the form of a chloroform solution from a Hamilton syringe, the stock solution being diluted stepwise immediately before introduction. The integrated ion current as measured by the area under the envelope of the peaks at *m/e* 351 was plotted against sample size and a straight line graph was obtained (Fig. 2). The limit of useful measurement was once again of the order of 10^{-12} g. For all measurements the source temperature was 255°.

Copper oxinate exists in an anhydrous form and as a dihydrate which is stable up to a temperature of 60°. The sample examined had previously been dried at a temperature of 110° and was in the anhydrous form. The mass spectrum showed no peaks which

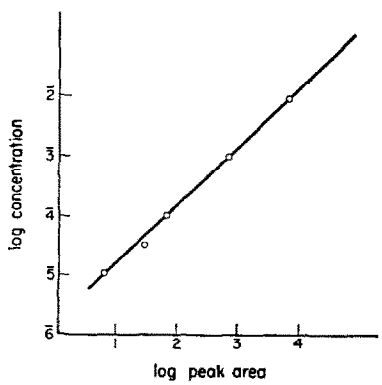

FIG. 2.—Variation of integrated ion current with weight of copper oxinate.

could have been derived from the evaporation of the copper oxinate as its dihydrate. The anhydrous form is reported to be stable up to a temperature of 300° which is nearly 50° above the temperature at which evaporation took place.

Zinc oxinate

The mass spectrum of zinc oxinate is illustrated in Fig. 3. There is an intense mass peak at *m/e* 352 corresponding to a metal:ligand ratio of 1:2. Although it is not visible in the figure, on close examination of the original record a smaller peak is revealed at *m/e* 560 corresponding to a metal:ligand ratio of 2:3. There is thus some evidence for the existence of more than one zinc oxinate species and it would be

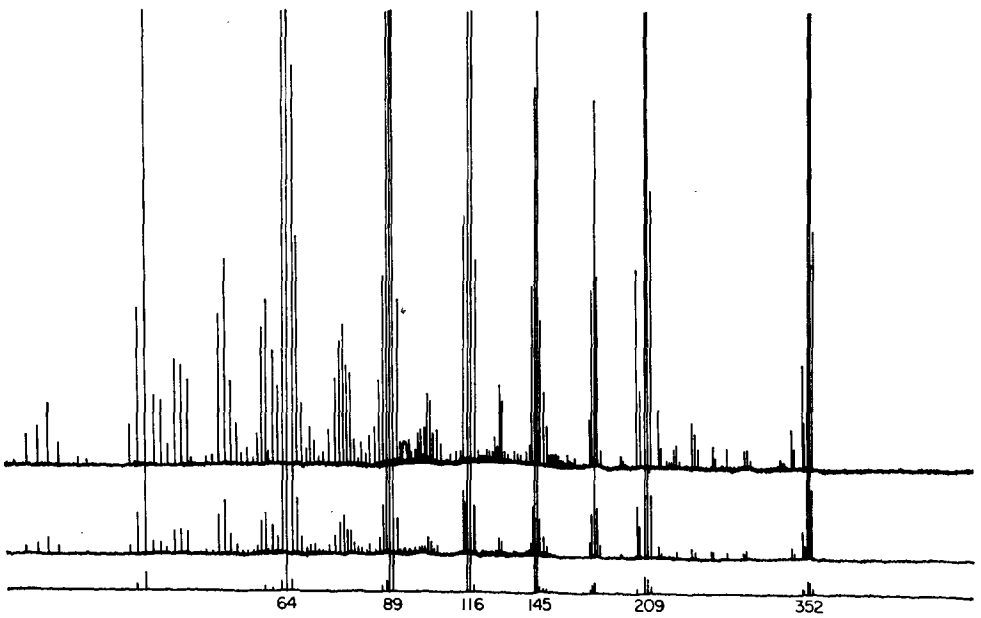

FIG. 3.—Mass spectrum of zinc oxinate.

expected that the two chelates would evaporate at different rates. It is not therefore possible to make a direct correlation between the integrated ion current at *m/e* 352 and zinc content in a sample. The envelope of the peaks at *m/e* 352 does in fact show two separate maxima the first of which may correspond to the molecule ion containing two oxinate residues and the second to a fragment ion of the same composition derived from decomposition products of higher molecular weight such as that containing three oxinate residues (Fig. 4). The sensitivity obtained as expressed by the peak area for a given weight of zinc oxinate was much lower than that found for other metal chelates and the smallest sample size examined was 5×10^{-8} g. This low sensitivity may be due to the complication of the existence of more than one metal chelate species or may be due to incomplete evaporation or to evaporation with decomposition. It is significant that no ion current at *m/e* 352 is recorded below a source temperature of 380°.

The sample was dried at 100° and the composition at this temperature is reported to be $ZnOx_2.1\frac{1}{2}H_2O$. The compound becomes anhydrous at 160° and the mass

spectrum reveals no peaks which could be attributed to the hydrated form. It is significant that the anhydrous form is reported to decompose at 300°, and evaporation was not observed by us until a temperature of 380° was reached. Thus, the low sensitivity and the appearance of mass peaks due to ions containing more than one zinc atom may be due to a polymerization process.

Aluminium oxinate

The mass spectrum of aluminium oxinate was recorded by evaporation of a solid sample at a temperature of 400°. The spectrum illustrated in Fig. 5 shows an intense

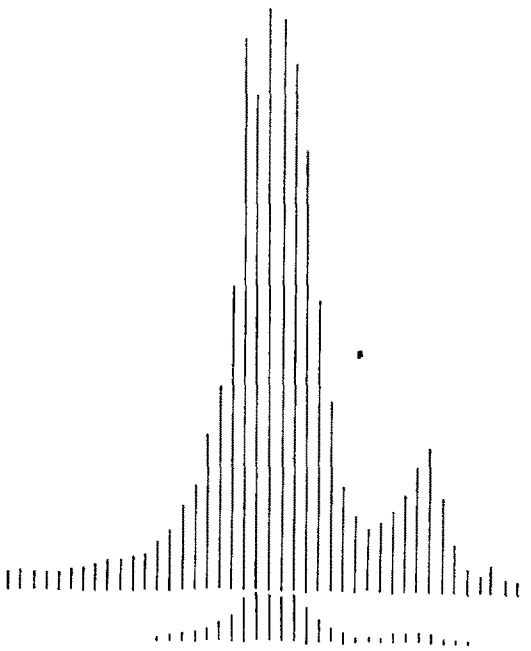

FIG. 4.—Integrated ion current curve for zinc oxinate.

peak at *m/e* 459 corresponding to the molecule ion $Al(Ox)_3^+$ but as there was no convenient reference peak close to this *m/e* value, the peak corresponding to the fragment ion $Al(Ox)_2^+$ was selected for quantitative study. The integrated ion current curves were recorded for a series of sample sizes and the limit of detection was found to be 10^{-10} g. It is possible that some decomposition may occur at the high source temperature used. The sample used was dried at 110° and was anhydrous, but this form is reported to begin to decompose at 375° and to form alumina at 700°. However, no mass peaks corresponding to ions containing more than one aluminium atom were observed.

Iron(III) oxinate

Under the conditions used for the precipitation of iron oxinate it has been suggested[2] that both iron(II) and iron(III) oxinates are produced. The mass spectrum illustrated in Fig. 6, recorded for evaporation of the solid sample at a temperature of 405°, contains an intense peak at *m/e* 344 corresponding to the ion $^{56}Fe(Ox)_2^+$ and

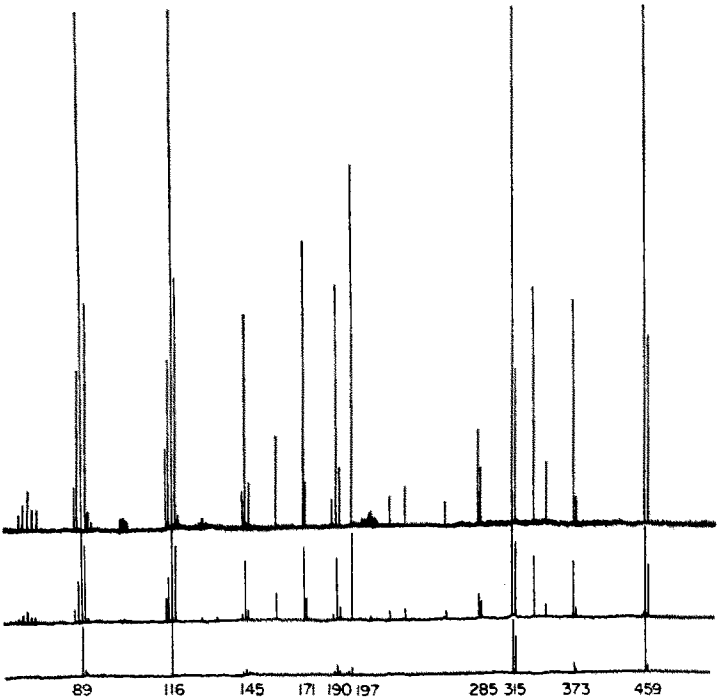

FIG. 5.—Mass spectrum of aluminium oxinate.

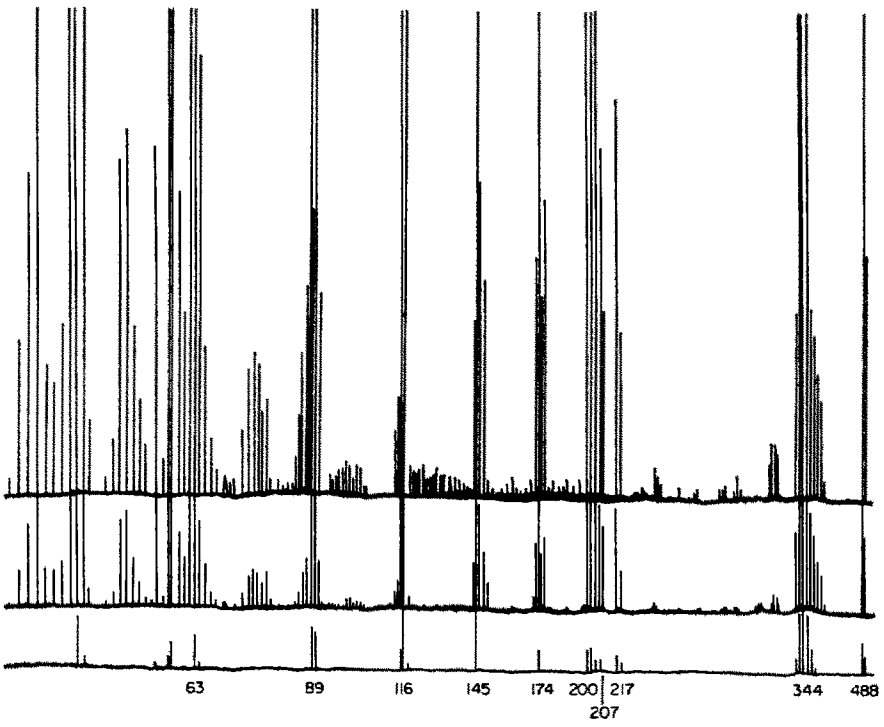

FIG. 6.—Mass spectrum of iron oxinate.

a smaller peak at *m/e* 488 corresponding to the ion $^{56}Fe(Ox)_3^+$. The relative proportions of the two species were not determined because of the intractable nature of the precipitate, which was fairly insoluble. A very dilute solution in dioxan could be prepared and 1 μl of this solution gave a small integrated ion current curve on evaporation in the instrument. It was estimated that the concentration in dioxan was of the order of a few ppm.

At the temperature used to dry the sample, iron(III) oxinate is reported to be anhydrous, but it appears certain that substantial decomposition was taking place at the evaporation temperature of 405°, as the upper limit of stability of the anhydrous form is given as 284°.

Other metals

The oxinates of nickel, manganese and cobalt are not soluble in the solvents used for the other metal chelates but are soluble in dimethyl sulphoxide. Despite the fact that the solid samples of the three metal chelates gave on evaporation mass spectra which could be readily interpreted, when dimethyl sulphoxide solutions were used in the manner described above not only could no integrated ion current curves be obtained but the normal mass spectra were not exhibited on evaporation. The spectrum recorded showed no peaks due to ions containing metal atoms, this observation being confirmed by high resolution mass measurement. It appears that there is some strong interaction or chemical change on dissolution in dimethyl sulphoxide. It was not possible, therefore, to carry out quantitative studies on these metal oxinates, but their mass spectra were recorded by the evaporation of small solid samples. The sample of nickel oxinate used was partly hydrated, having been dried at 110°. The anhydrous form is reported to be stable between 130° and 340°. The mass spectrum which was recorded at an evaporation temperature of 370° exhibits an intense mass peak corresponding to the ion $Ni(Ox)_2^+$.

The sample of cobalt oxinate was dried at 100°. At room temperature cobalt oxinate dihydrate is stable, but at temperatures below 130° the composition is closer to $Co(Ox)_2.1\frac{1}{2}H_2O$. Decomposition occurs above 306° but evaporation was not observed until the source temperature was raised to 370°. The mass spectrum is illustrated in Fig. 7 and in addition to an intense peak at *m/e* 347 corresponding to the molecule ion $^{59}Co(Ox)_2^+$, there was a smaller peak at *m/e* 406 corresponding to the ion $^{59}Co_2(Ox)_2^+$.

The sample of manganese oxinate used was dried at 110° and was most probably the dihydrate, which is reported to be stable up to a temperature of 150°. The anhydrous form decomposes at 250° but evaporation was not observed until 360°. The mass spectrum (Fig. 8) was complicated, showing peaks at *m/e* 542 and 487 which corresponded to the ions $^{55}Mn_2(Ox)_3^+$ and $^{55}Mn(Ox)_3^+$, in addition to a large peak at *m/e* 343 corresponding to the molecule ion $^{55}Mn(Ox)_2^+$.

Magnesium oxinate exists as the dihydrate at the temperature of drying (100°) but becomes anhydrous between 160° and 200°. The anhydrous form begins to decompose at 345°. Evaporation begins at 370°, when the mass spectrum reveals a peak at *m/e* 312 corresponding to the ion $^{24}Mg(Ox)_2^+$ and two unidentified peaks at *m/e* 343 and 346 which do not appear to be due to the dihydrate. On raising the temperature to 400° the peak at *m/e* 312 becomes more intense and a new peak appears

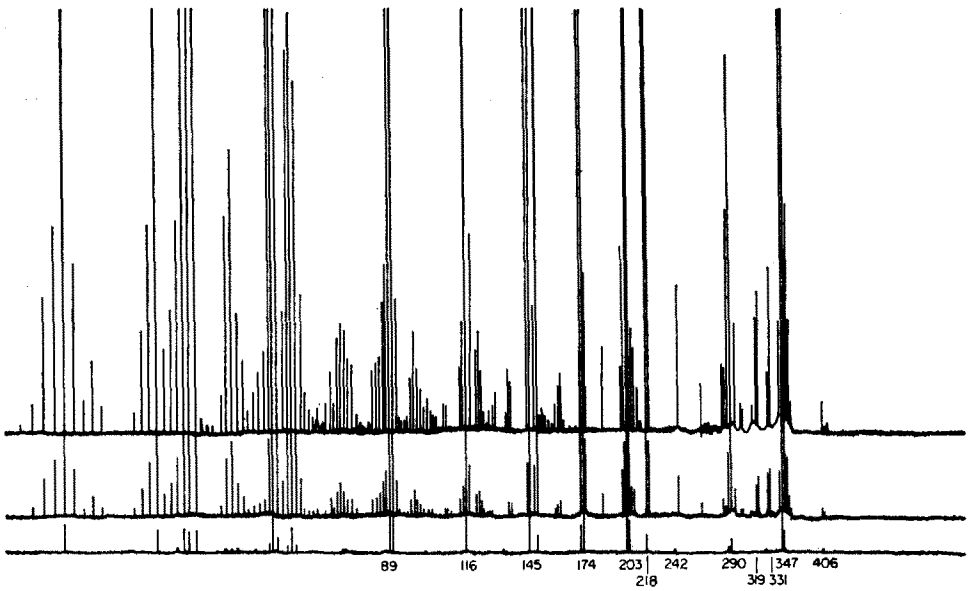

FIG. 7.—Mass spectrum of cobalt oxinate.

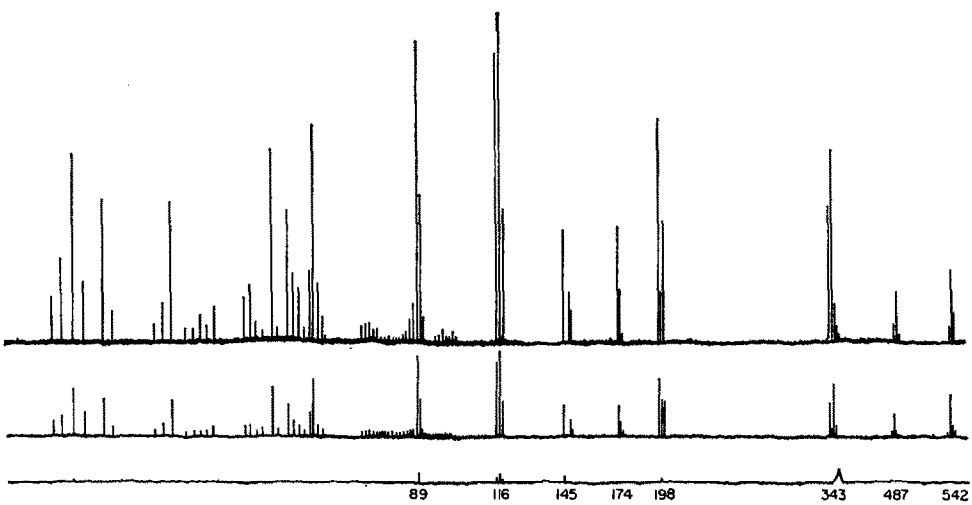

FIG. 8.—Mass spectrum of manganese oxinate.

at *m/e* 480 corresponding to the ion $^{24}Mg_2(Ox)_3^+$. It seems probable that this is due to a decomposition process taking place in the solid phase.

Determination of mixtures

Because of the differences between the molecular weights of the metal complexes it should be possible to record the integrated ion current curve corresponding to one metal chelate in the presence of others. In fact the molecule ion peak in the mass spectrum is the most specific detectable physical property. In mixtures of metal chelates, therefore, it should be possible to determine each component in a mixture by

making a separate introduction and recording. A further possibility was the determination of the components of the mixture in a single introduction by making use of the difference in the temperature of evaporation. To test this possibility 1 μl of each of the standard 0·01% solutions of copper and aluminium oxinates were introduced simultaneously. When the temperature was raised to 255° the integrated ion current at *m/e* 351 corresponding to the ion $^{63}Cu(Ox)_2^+$ could be recorded. When however the temperature was raised to 400° no signal could be recorded at *m/e* 315 corresponding to the ion^{27} $Al(Ox)_2^+$. If however the sample mixture was introduced and the source temperature raised directly to 400° then the integrated ion current could be recorded normally at *m/e* 315. This phenomenon may be explained by assuming that the instrument detects only the rapid evaporation of the sample and that slow evaporation of the less volatile sample occurs undetected at the lower temperature. There are some preliminary indications that the sensitivity also changes when a second metal chelate is present but further work is required to assess the extent of this interaction between the components of the mixture.

CONCLUSIONS

1. The oxinates of copper, aluminium, zinc, iron, cobalt, manganese, nickel and magnesium are sufficiently volatile at temperatures between 255° and 405° for their mass spectra to be recorded.

2. In all spectra recorded, the peak corresponding to the expected molecule ion was sufficiently intense to permit its use in quantitative determination. In some cases, however, it was more convenient to use a fragment peak at a lower *m/e* value.

3. There was evidence for the existence of ions of the type $M_2(Ox)_3^+$ (where M is a bivalent metal) where the vaporization temperature is higher than the decomposition temperature. It is suggested that these peaks result from a polymerization process taking place in the solid phase.

4. The technique may be applied successfully to the estimation of submicrogram quantities of copper and aluminium oxinates. While each metal may be detected separately, in a mixture of the two, there is evidence of mutual interference in the determination of the two chelates.

Acknowledgements—The authors are indebted to Dr. W. I. Stephen for his interest and advice and to the Science Research Council for a grant to purchase equipment.

Zusammenfassung—Die Massenspektren der Oxinate von Zink, Eisen(III), Mangan(II), Nickel, Kobalt, Aluminium, Kupfer und Magnesium wurden gemessen. Die Konzentrationen mehrerer dieser Chelate wurden zu den integrierten Ionenströmen in Beziehung gesetzt, die bei einem charakteristischen *m/e*-Wert während des Verdampfens der Probe in der Ionenquelle eines M.S. 9-Massenspektrometers von A.E.I. registriert wurden. Diestrukturelle Bedeutung einiger der Massenspektren wird diskutiert.

Résumé—On a mesuré les spectres de masse des oxinates de zinc, fer(III), manganèse(II), nickel, cobalt, aluminium, cuivre et magnésium. On a établi un rapport entre les concentrations de plusieurs de ces chélates et les courants d'ions intégrés enregistrés à une valeur *m/e* significative durant l'évaporation de l'échantillon dans la source d'un spectromètre de masse A.E.I. M.S.9. On discute de la signification structurale de quelques-uns des spectres de masse.

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CO-ORDINATING PROPERTIES OF SOME LIGAND SYSTEMS RELATED TO 4-(2-PYRIDYLAZO)RESORCINOL

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Summary—The metal-complexing properties of 2-(8-quinolylazo)-1-naphthol-4-sulphonic acid and the 2-pyridyl-, 2-pyrimidyl- and 8-quinolylhydrazones of salicylaldehyde have been described and compared with those of 4-(2-pyridylazo)resorcinol and related dyes. The sensitive chromophoric action of metal ions on the latter group of dyes is thought to be due to the formation of a resonance-stabilized anion in which the heterocyclic nitrogen atom plays an important part. Ligands capable of forming chelates containing larger rings give on reaction with metals less sensitive colour reactions but more stable complexes.

THE use of azo dyestuffs containing a heterocyclic nitrogen atom and hydroxyl group *o-o'* to the azo group is now very familiar in analytical chemistry.[1] Of such dyes, 1-(2-pyridylazo)-2-naphthol (PAN) and 4-(2-pyridylazo)resorcinol (PAR) are by far the most important. Certain other azo dyes of pyridine and a wide range of the easily prepared thiazolylazo dyestuffs have also been studied as analytical reagents, but more briefly.[1] We have made a critical comparison of the analytical potentials of pyridineazo and pyrimidineazo dyestuffs,[2,3] and have shown that the latter dyes possess several advantages over the former as analytical reagents.

The two main features of the PAR or PAN chelating system are the wide range of metals capable of being complexed by these dyes and the large and characteristic bathochromic shifts accompanying this complex formation.

We have studied the metal-complexing properties of a series of compounds related to PAR.[4–6] However, in each compound, one or more of the potential co-ordinating groups of PAR has been blocked out. We have thus been able to show that dyes of this type act as tridentate chelating agents, mainly through the heterocyclic nitrogen atom, the azo nitrogen atom nearest to the phenol ring, and the *o*-hydroxyl group. In this way, the ligands form two five-membered rings on chelation.

We now report the preparation and metal-complexing properties of a new series of ligands capable of forming metal chelates in the same manner as PAR, but owing to the geometry of the ligand molecules, forming either a six-membered and a five-membered or two six-membered ring systems on chelation. The systems studied include an 8-quinolylazo derivative and some heterocyclic hydrazones of salicylaldehyde (see formulae at top of next page).

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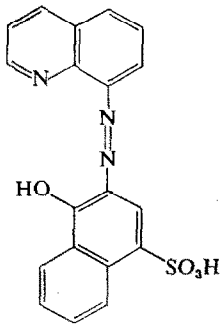
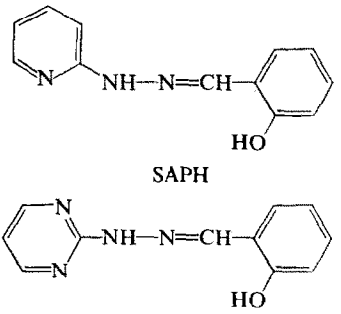
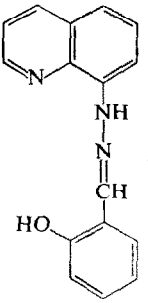


QANα4S



SAPH SAMH



SAQH

EXPERIMENTAL

Spectroscopic and potentiometric measurements

The techniques used to measure the stability constants and electronic spectra of the dyes and their complexes have been described previously.[6] The potentiometric titration technique was based on that of Irving and Rossotti.[7] All measurements were made in 50% aqueous methanolic solutions at an overall ionic strength of 0·1 (adjusted with sodium perchlorate) and a temperature of 25° (potentiometric) or 20 ± 2° (spectrophotometric).

2-(8-*Quinolylazo*)-1-*naphthol*-4-*sulphonic acid* (*QAN*α*4S*)

Sodium 1,2-naphthoquinone-4-sulphonate (2·6 g) was dissolved in 1*M* hydrochloric acid (100 ml), to which was added a solution of 8-hydrazinoquinoline (1·6 g; prepared by the method of Krasavin *et al.*[8]) in ethanol (25 ml). The crude dye that was precipitated was purified by dissolving it in sodium hydroxide solution and reprecipitating with hydrochloric acid. The dye thus obtained was found to be homogeneous by thin-layer chromatography[9] and was assumed to be the 2-azo-1-naphthol isomer (*cf.* reference 2). Found: C, 53·4%; H, 4·3%; N, 9·6%. Calc. for $C_{19}H_{13}N_3O_4S.2\frac{1}{2}H_2O$: C, 53·7%; H, 4·2%; N, 9·9%.

Salicylaldehyde-2-pyridylhydrazone (*SAPH*)

Salicylaldehyde (5·1 ml) was added to a solution of 2-hydrazinopyridine (4·1 g; prepared by the method of Fargher and Furness[10]) in ethanol (25 ml). The solid formed was recrystallized from ethanol to give slightly off-white needles, m.p. 217·5–218·5°. Found: C, 67·7%; H, 5·4%; N, 19·8%. Calc. for $C_{13}H_{11}N_3O$: C, 67·6%; H, 5·2%; N, 19·7%.

Salicylaldehyde-2-pyrimidylhydrazone (*SAMH*)

Salicylaldehyde (2 ml) in ethanol (10 ml) was added to a solution of 2-hydrazinopyrimidine (1·1 g; prepared by the method of Shirakawa *et al.*[11]) in ethanol (15 ml). The solid formed was recrystallized from ethanol to give slightly off-white platelets, m.p. 213–4° (lit. 213–5°).[12] Found: C, 61·9%; H, 5·4%; N, 26·4%. Calc. for $C_{11}H_{10}N_4O$: C, 61·7%; H, 4·7%; N, 26·2%.

Salicylaldehyde-8-quinolylhydrazone (*SAQH*)

Salicylaldehyde (4 ml) in ethanol (20 ml) was added to 8-hydrazinoquinoline (3·3 g) in ethanol (40 ml). The solid formed was recrystallized from ethanol to give cream platelets, m.p. 150–1°, that slowly turned pink on exposure to light. Found: C, 74·0%; H, 5·5%; N, 16·1%. Calc. for $C_{16}H_{13}N_3O$: C, 73·0%; H, 4·9%; N, 16·0%.

Metal complexes of SAPH

These were prepared by mixing together alcoholic solutions of SAPH and a metal salt, from which the complex was precipitated without difficulty (see Table I).

RESULTS AND DISCUSSION

These ligands have been reported previously as chromatographic spray reagents.[13] The most striking difference between these new compounds and the ligands forming

TABLE I.—THE SOLID METAL COMPLEXES OF SAPH

Ion	Preparation		Found			Calculated			Formula L = $C_{12}H_{10}N_3O$	Colour
	Metal salt	Molar ratio	%C	%H	%N	%C	%H	%N		
Zn(II)	$Zn(CH_3CO_2)_2$	1:1	55·6	4·2	16·2	55·7	4·4	16·3	$ZnL_2.1\frac{1}{2}H_2O$	Yellow
Cu(II)	$CuCl_2$	1:1	41·0	4·0	11·8	41·5	4·0	12·1	$CuL.Cl.2H_2O$	Green
Co(II)	$CoCl_2$	1:2	52·2	4·3	14·7	52·4	4·1	15·2	$Co_2L_3.Cl.2H_2O$	Green
Fe(III)	$FeCl_3$	1:2	53·0	4·7	15·3	52·3	4·4	15·2	$FeL_2.Cl.2H_2O$	Black

two five-membered chelate rings (*e.g.*, PAR and PAN) is the very much smaller colour change produced on chelate formation by the former. QANα4S itself has a pink colour and its complexes are coloured blue, green and brown, but the contrast is poor. The dye, however, shows up most metals under ultraviolet light, and for this reason it is believed that QANα4S, like PAR and PAN, is non-selective in its reactions with metals. SAPH and SAMH have very similar properties to each other as chromatographic spray reagents. The backgrounds are colourless and the metal complexes stand out with varying shades of yellow. The vanadium complex is orange and the iron and ruthenium complexes are brown. The reagents appear to react with a wide range of metals, although the sensitivity is low for metals in groups Ia, IIa and IIIa. SAQH produces a cream background and very weak maroon to brown spots with only a limited number of metals in group VIII. It also produces a strong maroon colour with copper.

Tables II and III contain data relating to the electronic absorption spectra and acid dissociation constants of the ligands. All the hydrazone derivatives show bathochromic shifts on both protonation and ionization. Only with protonation of SAQH, however, is there a marked colour change (from pale cream to orange). QANα4S is interesting in that it shows small hypsochromic shifts on both protonation and ionization.

TABLE II.—SPECTRA OF THE LIGANDS

	Cation			Neutral molecule			Anion		
	pH	λ_{max} mμ	$\varepsilon \times 10^{-3}$	pH	λ_{max} mμ	$\varepsilon \times 10^{-3}$	pH	λ_{max} mμ	$\varepsilon \times 10^{-3}$
SAPH	1	357	22·5	7·5	337	21·8	13·5	363	17·8
SAMH	1	345	21·8	7·5	324	19·2	13·5	366	19·0
SAQH	1	456 323	4·9 15·4	7·5	376	19·0	13·5	400	15·0
QANα4S	0	460 352	11·0 11·3	5	508	19·8	13	495	14·4

TABLE III.—ACID DISSOCIATION CONSTANTS OF THE LIGANDS

	pK_{NH}	pK_{OH}
SAPH	5·08*	10·87†
SAMH	2·92*	10·20*
SAQH	2·27*	10·67†
QANα4S	1·79†	10·35†

* Determined potentiometrically.
† Determined spectrophotometrically.

The SAPH molecule may be compared with the 2-(2-pyridylazo)phenol molecule[6] in which the azo group has been replaced with the hydrazone group. Apart from increasing the chelate ring size, this group decreases the conjugation in the molecule, thus destroying its properties as a dye. Furthermore, SAPH may be considered as a simple derivative of 2-aminopyridine, which has a very high pK_{NH} value (6·86) because of resonance stabilization.[14] In the same way, the pK_{NH} of SAPH has a very much higher value than that of 2-(2-pyridylazo)phenol[6] (1·85). Owing to the increased basicity of the hydrazone link the phenolic proton is more strongly hydrogen-bonded, thus its pK_{OH} value is raised from 9·42 for 2-(2-pyridylazo)phenol[6] to 10·87 for SAPH. The behaviour of SAMH is similar [pK_{NH} and pK_{OH} of 2-(2-pyrimidylazo)phenol being 0·0 and 8·66 respectively[15]]. SAQH also has a high pK_{OH} value, presumably because of the existence of a strong internal hydrogen bond. Its pK_{NH} value, however, is low and this is probably due to the so-called "ortho-effect" (*cf.* the pK_{NH} of 8-aminoquinoline[14]).

Tables IV and V present data pertinent to the metal complexes of these four ligands. Some data collected under the same conditions are also included for 2-(2-pyridylazo)-phenol (*o*-PAP)[6], 2-(2-pyrimidylazo)phenol (*o*-MAP)[15] and 2-(2-pyridylazo)-1-naphthol-4-sulphonic acid (PANα4S)[2] for comparison purposes. No data could be obtained concerning the copper complexes of QANα4S or SAQH as these are completely insoluble in aqueous solvents. However, the precipitates of the copper complexes showed a metal-to-ligand ratio of 1:1 for both ligands. Precipitation also prevented log K_2 from being obtained for the zinc and cobalt complexes of SAPH. The log K_1 values for the iron(II) and nickel complexes of QANα4S were too large to be obtained by the Irving and Rossotti[7] technique. In fact, all that was seen from the titration was the formation of a 1:2 complex from a 1:1 complex. With cobalt(II) and QANα4S there was evidence of 1:1 chelate formation only. This is somewhat surprising, since the iron(II) and nickel complexes have 1:2 stoichiometry. If, in fact cobalt(II) does form a 1:2 complex and is then oxidized to cobalt(III), with the subsequent reduction of hydrogen ions, the net result on the titration figures would be the release of one proton only per cobalt atom, or apparently 1:1 complex formation.

Comparison of the spectra and stability constants of the complexes with the corresponding 5-5 ring complexes shows clearly two facts.

1. The large and characteristic bathochromic shifts associated with the formation of the 5-5 ring complexes are lost when the ring size is increased. QANα4S produces small bathochromic shifts with most metals, but the colour changes are clear to see with iron(II) and cobalt ions only. The bathochromic shift on the formation of the copper SAPH complex is about 50 mμ, as opposed to about 180 mμ for the corresponding *o*-PAP complex. Solubility problems restricted the data obtained for the metal complexes of the hydrazones, however, and the small colour changes associated with these ligands are best appreciated in a qualitative way when they are used as spray reagents. The small bathochromic shifts of the hydrazone complexes are probably due in part to the different chromophoric properties of the non-conjugated hydrazone link and to the non-planar nature of the ligand. This is not so, however, for the complexes of QANα4S, which contain the same chromophoric groups as do the PANα4S complexes.

2. The stabilities of the 5-6 ring complexes are considerably higher than those of the corresponding 5-5 ring complexes. This is clearly evident from the log K_1 values,

TABLE IV.—VISIBLE SPECTRA OF THE METAL COMPLEXES

Ligand	Metal	M:L;pH	λ_{max} mμ	$\varepsilon \times 10^{-3}$	Ligand	Metal	M:L;pH	λ_{max} mμ	$\varepsilon \times 10^{-3}$
QANα4S	Zn(II)	1:1;9	520–540	19·2	PANα4S	Zn(II)	1:1;9	528	26·0
	Ni(II)	1:1;9	525	18·0		Ni(II)	1:2;9	563	41·8
								532	45·8
	Co(II)	1:1;9	560	10·4		Co(III)	1:1;5	615	11·5
			418	8·4				583	12·8
	Pd(II)	1:1;9	512	21·6		Pd(II)	1:1;5	650	11·5
								612	12·9
	Fe(II)	1:1;9	496	15·4					
SAPH	Cu(II)	1:1;5	388	12·5	*o*-PAP*	Cu(II)	1:1;5	557	10·5
SAMH	Cu(II)	1:1;5	385	9·3	*o*-MAP†	Cu(II)	1:1;5	567	10·7

* 2-(2-pyridylazo)phenol.
† 2-(2-pyrimidylazo)phenol.

TABLE V.—STABILITY CONSTANTS OF THE METAL COMPLEXES

Ligand	Metal	log K_1	log K_2	log β_2	Ligand	Metal	log K_1	log K_2	log β_2
QANα4S	Zn(II)	10·6*	7·2*	17·8	PANα4S	Zn(II)	8·6*	8·5*	17·1
	Ni(II)		9·3*						
	Co(II)	10·5*							
	Fe(II)		9·4*						
	Mn(II)	8·6*	7·0*	15·6		Mn(II)	5·9*	6·1*	11·9
SAPH	Zn(II)	11·1*			*o*-PAP	Zn(II)	8·8*	8·1*	16·9
	Cu(II)	17·9†	5·9*	23·8		Cu(II)	13·8†	7·7*	21·5
	Ni(II)	13·8*	11·3*	25·1		Ni(II)			22·8†
	Co(II)	12·1				Co(II)	8·9*	9·3*	18·2
SAMH	Zn(II)	9·2*	7·1*	16·3	*o*-MAP	Zn(II)	7·6*	5·4*	13·0
	Cu(II)	16·0†	7·0*	23·0		Cu(II)	12·6†	6·6*	19·2
	Ni(II)	10·7*	8·1*	18·3		Ni(II)			21·0†
	Co(II)	10·4*	8·6*	19·0		Co(II)	5·6*		
	Fe(II)	9·9*	8·6*	18·5		Fe(II)			24·1†
SAQH	Ni(II)	~ 7*							
	Co(II)	6·3*	5·4*	11·7					

* Determined potentiometrically
† Determined spectrophotometrically

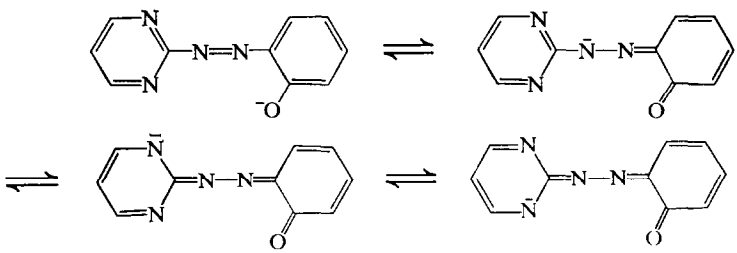
but is not quite so evident from the log K_2 values. From stereochemical considerations it can be seen that the increased stabilities of the 1:1 complexes do not arise from the shapes of the molecules. However, the gaps between the log K_1 and log K_2 values are larger for the new ligands and are thought to be evidence of the greater difficulty in packing two of these larger and more awkwardly shaped molecules around a metal atom. These two facts can be appreciated better when models of the ligands are studied.

It is seen that the Irving-Williams order of stabilities[16] is obeyed by these ligands with respect to log K_1. The order fails for log K_2 because of the reluctance of copper to form a 1:2 complex with tridentate ligands. The order for log K_1 holds even for the iron(II) complex. This is not so in the case of 2-(2-pyridylazo)phenol[6] which with iron(II) forms an abnormally stable, presumably low spin, complex. The nickel complex of SAMH appears to possess lower stability than would be expected by comparison with the other complexes. There is at present no satisfactory explanation of this fact.

Potentiometric titrations with iron(II)–SAQH and zinc–SAQH failed owing to the fact that hydrolysis of the metal ion occurred before complex formation. Although no

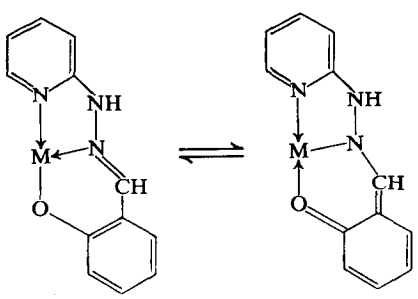
stability constants were thus obtained, it must be assumed from this fact that the complexes of SAQH, which will contain two six-membered chelate rings, are very much less stable than those of SAPH or 2-(2-pyridylazo)phenol. This is certainly so for the nickel and cobalt complexes for which some stability constants were obtained. SAQH possesses a very awkward shape for complex formation, the rings being bent almost at right angles to one another in the final complex. This fact must outweigh any other in determining the stability of the complexes of this ligand.

The greater stability of the 5-6 ring complexes, together with the small bathochromic shifts produced on their formation is thought to be caused directly by the ionization of the phenol group. The Irving-Rossotti theory assumes that it is the anion so produced that is in fact the chelating species and will therefore be mainly responsible for the properties of the complex. If the negative charge on this anion is delocalized over the whole molecule, then this will stabilize the anion and reduce its tendency either to protonate or form complexes. At the same time, the absorption peak of the resonance-stabilized anion is likely to move to longer wavelengths with respect to the neutral molecule if the resonance is more efficient. This resonance can take place in the anion and the complex but not in the neutral molecule, because of the unique properties of the unshielded proton. Very favourable canonical forms can be written for the 2-(2-pyridylazo)phenol anion and its pyrimidyl analogue:



With QANα4S and the hydrazones it is not possible for the negative charge to be delocalized onto the electronegative heterocyclic nitrogen atoms. It will therefore remain more closely associated with the oxygen atom and give rise to more stable complexes. The perturbation of the molecule being less, however, the bathochromic shifts involved will also be smaller.

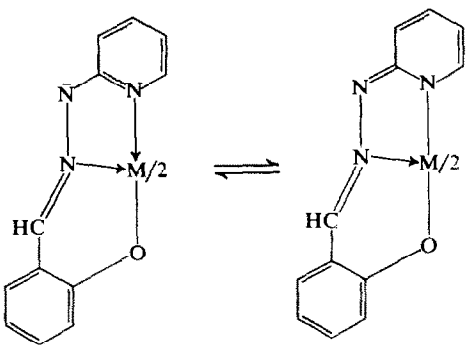
Another factor that may be responsible for the higher stabilities of these complexes is the possibility of resonance in the six-membered chelate ring. For example, with a chelate of SAPH, the following canonical forms are possible:



Ring stabilization through resonance of this kind is not possible for the complexes of PAN-type ligands, since they do not contain six-membered chelate rings. There are

two objections to this picture, however: (*i*) if the *o*-quinonoid structure played any significant role in the overall structure of the hydrazone chelates, then we would expect a deeper colour due to the presence of the *o*-quinone chromophore, but (*ii*) this explanation cannot be extended to account for the difference in pK_{OH} values between the two types of ligands, since the hydroxyl proton can be hydrogen-bonded into a six-membered ring with equal felicity in all the ligands studied.

The solid metal complexes of SAPH show some interesting properties in strongly alkaline medium. Normally the action of alkali on a metal complex of a heterocyclic azo dyestuff is to cause it to dissociate into the ligand anion and the metal hydroxide. The action of alkali on the complexes of SAPH is shown in Table VI. With the exception of zinc, all the complexes form strongly coloured water-soluble species. This is thought to be due to the removal of the hydrazine proton, which acquires acid properties on chelate formation. The resulting anion is capable of resonance stabilization involving a planar form of the ligand:



Similar behaviour to this is well known for pyridine-2-aldehyde-2-pyridylhydrazone and related ligands.[17]

In conclusion, it thus appears that the very sensitive chromophoric action of metals on dyes related to PAR and PAN is due to the formation of a resonance-stabilized anion in which the charge is partly located on the electronegative heterocyclic nitrogen atom. This is only possible in ligands forming five membered ring systems on chelation. Expansion of one of the chelate rings to six atoms increases the stability of the complexes because of the resultant greater localization of charge and the possible introduction of resonance into the six-membered chelate ring.

TABLE VI.—ACTION OF ALKALI ON THE CHELATES OF SAPH

Metal	Before the addition of sodium hydroxide		After the addition of sodium hydroxide	
	Soln. colour	Water solubility	Soln. colour	Water solubility
Zinc	Pale yellow	Insoluble	Pale yellow	Insoluble
Copper	Pale green	Slightly soluble	Orange yellow	Soluble
Cobalt	Yellow	Soluble	Brown	Soluble
Iron(III)	Dark brown (in alcohol)	Insoluble	Dark brown	Soluble

Zusammenfassung—Die Komplexbildungseigenschaften von 2-(8-chinolylazo)-1-naphthol-4-sulfonsäure und den 2-Pyridyl, 2-Pyrimidyl- und 8-Chinolylhydrazonen von Salicylaldehyd werden beschrieben und mit denen von 4-(2-pyridylazo)resorcin und verwandten Farbstoffen verglichen. Die empfindliche Chromophorwirkung von Metallionen bei der zultzt genannten Gruppe von Farbstoffen wird auf Bildung eines resonanzstabilisierten Anions zurückgeführt, in dem der heterocyckische Stickstoff eine wichtige Rolle spielt. Zur Chelatbildung befähigte Liganden mit großeren Ringen geben mit Metallen weniger empfindliche Farbreaktionen, aber stabilere Komplexe.

Résumé—On a décrit les propriétés complexantes vis-à-vis des métaux de l'acide 2-(8-quinolylazo)1-naphtol 4-sulfonique et des 2-pyridyl-, 2-pyrimidyl- et 8-quinolylhydrazones du salicylaldéhyde et les a comparées à celles du 4 (2-pyridylazo) résorcinol et des colorants apparentés. On pense que l'action chromophorique sensible des ions métalliques sur le dernier groupe de colorants est due à la formation d'un anion stabilisé par résonance dans lequel l'atome d'azote hétérocyclique joue un rôle important. Les ligands capables de former des chélates contenant de plus grands cycles donnent par réaction avec les métaux des réactions colorées moins sensibles mais des complexes plus stables.

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SPECTROPHOTOMETRIC STUDIES OF RUTHENIUM(III) AND RHODIUM(III)-OXIMIDOBENZOTETRONIC ACID COMPLEXES AND THE SIMULTANEOUS DETERMINATION OF THE TWO METALS

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Summary—Ruthenium(III) and rhodium(III) form stable coloured complexes in ethanolic solution with oximidobenzotetronic acid (OBTA). Ruthenium forms a purple-violet $Ru(OBTA)_3$ complex at pH 1·1–3·5, which is stable over the pH range 1·1–11·3. Rhodium(III) forms a yellowish-brown complex, $RhCl_3(OBTA)_2$, at pH 2–8; at higher pH (11·5 and above) the complex is reddish-brown, but has the same Rh:OBTA ratio. A method for the simultaneous determination of these two metals is proposed, and the interference by commonly occurring ions has been investigated.

THE red colour produced by the addition of tin(II) chloride forms the basis of the best method available for the colorimetric determination of rhodium;[1] thiourea and its derivatives[2] have been recommended for the colorimetric determination of ruthenium(III). Critical reviews on the use of these and other reagents, along with their modifications and extensions, for the colorimetric determination of rhodium(III) and ruthenium(III) have been given by Beamish.[3–5] More recently, nitroso-R-salt[6] and trifluorothenoylacetone[7] have been suggested for the colorimetric estimation of rhodium, and salicylic acid,[8] sulphosalicylic acid[8] and nitroso-R-salt[9] have been proposed for the spectrophotometric determination of ruthenium.

Oximidobenzotetronic acid (OBTA), α-isonitrosobenzotetronic acid or 3-nitroso-4-hydroxy-5,6-benzopyrone-2, has already been used for the spectrophotometric determination of cobalt[10] and iron,[11] and for the gravimetric determination of cobalt[12] and palladium.[13] During the course of the present investigations, it was found that an ethanolic solution of this reagent instantaneously forms a blue-black water-soluble complex with aqueous ruthenium(III) chloride solution, slowly changed at room temperature to purple-violet. This change is more rapid at 90–100°, being then complete in about 25 min. The purple-violet solution has an absorption maximum at 520 mμ, obeys the Beer-Lambert law over the concentration range 0·4–20·2 ppm of ruthenium(III), is formed over the pH range 2·0–5·5 and is stable for 48 hr. The molar composition of the complex is 1:3 (metal:ligand).

No colour change is noticeable when ethanolic OBTA solution is added to rhodium(III) solution [taken as chlororhodate(III)] at room temperature. On heating the solution in a boiling water-bath, however, a yellow-brown complex is slowly formed, which on addition of potassium hydroxide solution instantaneously becomes red-brown. The red-brown complex at pH 12·0 shows absorption maxima at 410 mμ and 475 mμ, while the yellow-brown solution formed at pH 5·0 has only one maximum at 385 mμ. The complex at pH 12·0 obeys the Beer-Lambert law at 475 mμ over the

concentration range 0·7–15·7 ppm of rhodium(III), its absorbance remaining unchanged for 4 hr. The metal to ligand ratio at both the wavelengths is 1:2. Ruthenium(IV) gives a colour reaction with OBTA only on prolonged heating, presumably by reduction to ruthenium(III) by the alcohol present.

Because the ruthenium(III) and rhodium(III) complexes with OBTA form at different pH values and have different absorption maxima, this reagent can be used for the simultaneous spectrophotometric determination of rhodium(III) and ruthenium(III).

EXPERIMENTAL

Reagents

Oximidobenzotetronic acid (OBTA). Prepared by the method described earlier[11] and used in freshly prepared ethanolic solution.

Rhodium(III) and ruthenium(III). Stock solutions were prepared by using potassium chlororhodite

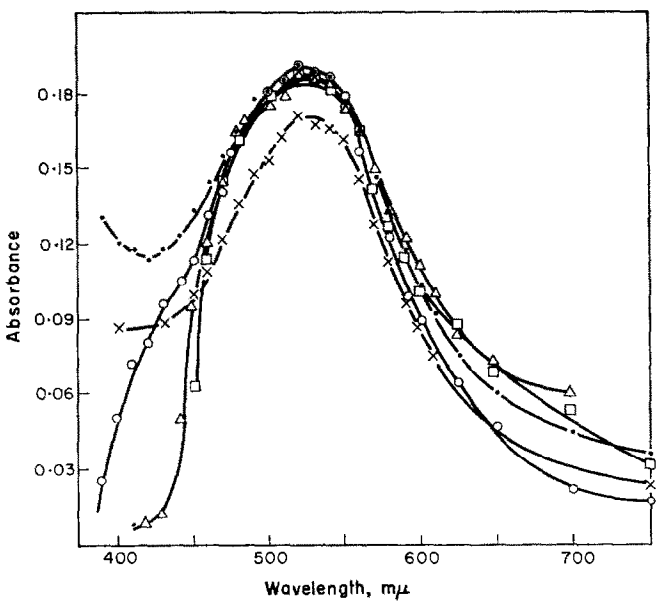


FIG. 1.—Absorption spectra of ruthenium(III)–OBTA complex at different pH values. Ru(III) 2·7 μg/ml; —×— pH; 1·1; —·— pH 2·0; —○— pH 3·5; —Δ— pH 10·1; —□— pH 11·8.

and ruthenium trichloride respectively (Johnson Matthey). They were standardized by spectrophotometric[1,3] and gravimetric methods.[14]

All other chemicals used were either from Johnson Matthey, or of B.D.H. AnalaR or Merck *pro analysi* quality.

Absorption spectra of ruthenium(III) and rhodium(III) complexes with OBTA

Ruthenium(III)–OBTA complex. A tenfold excess of reagent was added to ruthenium trichloride solution and the solution thus obtained was heated in a boiling water-bath for 25 min. This resulted in the formation of a purple-violet solution. The absorption spectrum of this complex, after adjustment of pH, was measured against reagent as blank in 1-cm² cross-section cylindrical tubes in a Unicam SP600. Within the pH range 1·1–11·3, the complex exhibited a single absorption maximum at 520 mμ (Fig. 1). As the reagent has negligible absorbance at this wavelength, all subsequent measurements were made at it.

Rhodium(III)–OBTA complex. Absorption spectra of the rhodium(III)–OBTA complex, obtained

by heating a tenfold excess of reagent with potassium chlororhodate(III) solution on a boiling water-bath for 45 min, were taken within the pH range 5·0–12·3, with the reagent solution as blank. At pH 5·0 the yellow-brown solution showed a single absorption peak at 385 mμ with negligible absorption at 475 mμ, (Fig. 2), while at pH 11·5 to 12·3, the red-brown solution showed two maxima, at 410 mμ and 475 mμ. For analytical determinations the wavelength 475 mμ was selected because at this wavelength both the reagent and rhodium(III) solutions have negligible absorbance.

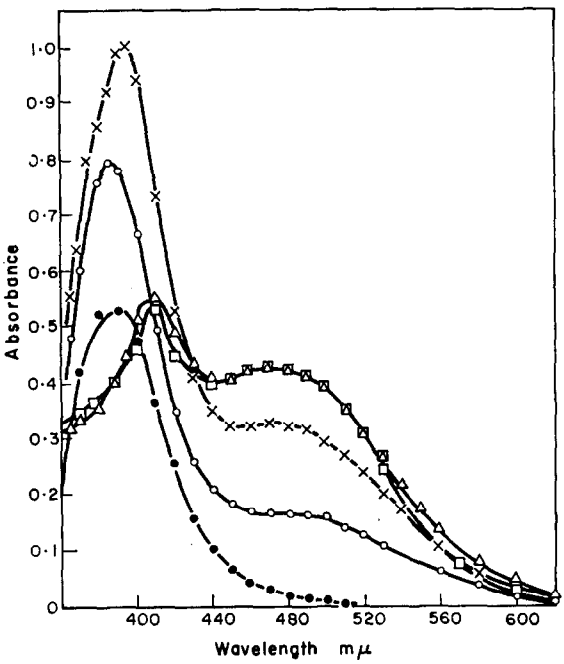


FIG. 2.—Absorption spectra of rhodium(III)–OBTA complex at different pH values Rh(III) 6·25 μg/ml —·— pH 5·0 —○— pH 9·4 —×— pH 10·0 —△— pH 11·6; —□— pH 12·4.

RESULTS AND DISCUSSION

Effect of time

Formation of the complexes. The colour development of the complexes is slow for both metals. The heating times required in a boiling water-bath for obtaining stable ruthenium(III) and rhodium(III) complexes were found to be 25 and 35 min respectively.

Stability of the complexes. At pH 3·5 the ruthenium(III)–OBTA complex formed as above does not show any significant change in its absorbance for up to 48 hr; the rhodium(III)–OBTA complex at pH 12·0 is stable for 4 hr at room temperature (≈30°). Eventually the solutions became opalascent.

Amount of reagent needed

It was observed that for ruthenium(III) the minimum ratio of reagent to metal required for full colour development is 5 and for rhodium(III) it is 3 (see Fig. 3). In the determinations, however, the ratio OBTA:metal was maintained at 10, as the excess of reagent has no significant effect on the absorbance of the complexes.

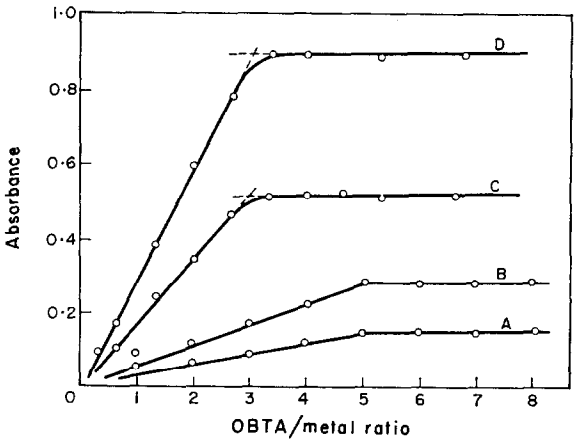


FIG. 3.—Effect of reagent concentration on the formation of Ru(III)- and Rh(III)-OBTA complexes.
A: Ru(III) 2·0 μg/ml *B*: Ru(III) 4·0 μg/ml *C*: Rh(III) 5·78 μg/ml; *D*: Rh(III) 12·49 μg/ml.

pH Effect

It was observed that the absorbance of the ruthenium(III)–OBTA complex at 520 mμ does not change over the pH range 1·3–11·7 (Table I), whereas for the rhodium(III)–OBTA complex at 475 mμ the optical density increases up to pH 11·5 and remains constant thereafter (Table II).

TABLE I.—EFFECT OF pH ON Ru–OBTA COMPLEX

pH	0·9	1·3	1·9	2·8	4·0	5·9	7·2	11·7	12·5
Absorbance at 520 mμ	0·133	0·138	0·140	0·139	0·138	0·140	0·139	0·140	0·126

Concentration of Ru(III) = 2·0 ppm.

TABLE II.—EFFECT OF pH ON Rh(III)–OBTA COMPLEX

pH	6·3	8·5	10·5	11·0	11·5	11·7	12·1	12·7
Absorbance at 475 mμ	0·005	0·013	0·043	0·055	0·065	0·066	0·066	0·065

Concentration of Rh(III) = 0·96 ppm.

Beer-Lambert law

The purple-violet ruthenium(III)–OBTA complex obeys the Beer-Lambert law at 520 mμ over the range 0·45–20·25 ppm ruthenium(III) with a molar absorptivity of $7·08 \times 10^3$; the sensitivity (Sandell) is 0·07 μg cm^{-2} for an absorbance of 0·005.

The red-brown rhodium(III)–OBTA complex obeys the Beer-Lambert law at 475 mμ, over the range 0·7–15·7 ppm rhodium(III) at pH > 11·5, the molar absorptivity being $7·06 \times 10^3$ and the sensitivity 0·07 μg cm^{-2}.

Extractability

The purple-violet Ru(III)–OBTA complex is not extracted from aqueous solutions by ether, benzene, toluene or nitrobenzene, but is partially extracted by chloroform

or cyclohexanol. The red-brown rhodium(III) complex at pH 12·0 is not extracted by any of the solvents mentioned.

Interference by foreign ions

It was found that oxalate, tartrate, citrate, borate, fluoride, phosphate, acetate and nitrite when present in quantities 100 times that of rhodium or ruthenium, and sulphate, nitrate or chloride in quantities up to 1000 times the amount of metal do not interfere. The limit of tolerance for cations commonly associated with these metals was determined and is in Table III.

TABLE III.—INTERFERENCE DUE TO FOREIGN IONS

Foreign ion	Ru(III)	Rh(III)	Pd(II)	Os(IV)	Ir(IV)	Pt(IV)	Fe(II)	Co(II)	Ni(II)
Maximum, *ppm*, tolerated for 1·4 ppm Ru(III)	—	50	4·8	2·2	2·1	11·0	0·5	0·05	112
Maximum, *ppm*, tolerated for 1·6 ppm Rh(III)		—	4·6	7·5		9·5			
2·0 ppm Rh(III)	0·02				0·8		11·2	0·05	112

Simultaneous determination of ruthenium(III) and rhodium(III)

Solutions containing various quantities of rhodium(III) and ruthenium(III) were mixed with excess of ethanolic OBTA solution and heated in a water-bath for 45 min. The absorbance of the solution at pH 3·5 was measured at 475 mμ and 520 mμ against a reagent blank; and again at pH 12·0 and 475 mμ.

The absorbance at 520 mμ and pH 3·5 was taken to be due to ruthenium(III) only, while the increase in the absorbance at 475 mμ on raising the pH of the solution to ~12 was attributed to rhodium(III) only. Some results are given in Table IV.

Molar composition

The composition of the Ru–OBTA complex was determined by Job's method of continuous variations[15] as modified by Vosburgh and Cooper,[16] with water as blank.

TABLE IV.—SIMULTANEOUS DETERMINATION OF RUTHENIUM(III) AND RHODIUM(III)

Taken, *ppm*		Absorbance at pH 3·5		Absorbance at pH 12	Diff. at 475mμ	Found, *ppm*		Error, *ppm*	
Ru	Rh	520 mμ	475 mμ	475 mμ		Ru	Rh	Ru	Rh
1·45	17·0	0·103	0·110	1·28	1·17	1·47	16·9	+0·02	−0·1
1·94	19·1	0·140	0·212	1·55	1·34	2·00	19·3	+0·06	+0·2
2·42	12·7	0·172	0·222	1·17	0·95	2·46	13·7	+0·04	+1·0
2·42	10·8	0·174	0·224	0·990	0·766	2·49	11·1	+0·07	+0·3
2·90	17·0	0·211	0·244	1·42	1·18	3·01	17·0	+0·11	±0·0
2·90	8·48	0·214	0·245	0·840	0·595	3·06	8·58	+0·16	+0·10
3·39	6·36	0·232	0·254	0·698	0·444	3·31	6·40	−0·08	+0·04
5·81	4·24	0·398	0·408	0·705	0·297	5·69	4·28	−0·12	+0·04
7·26	2·12	0·505	0·515	0·670	0·155	7·21	2·23	−0·05	+0·11
3·39	6·36	0·235	0·257	0·698	0·441	3·36	6·36	−0·03	±0·0

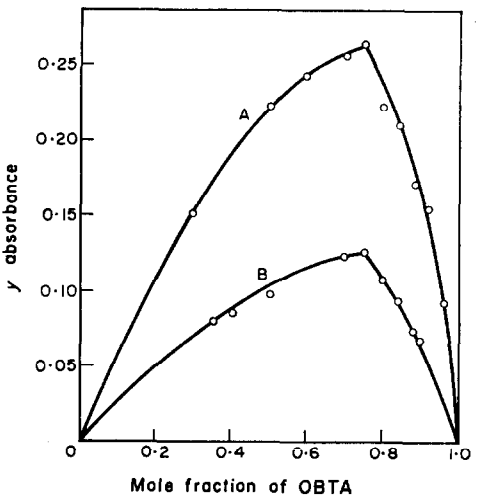


FIG. 4.—Job's curves for Ru(III)–OBTA system at pH 3·5 and wavelength 520 mμ. Total concentration of Ru(III) and OBTA for curve $A = 3{\cdot}64 \times 10^{-4}M$ and for curve $B = 2{\cdot}18 \times 10^{-4}M$.

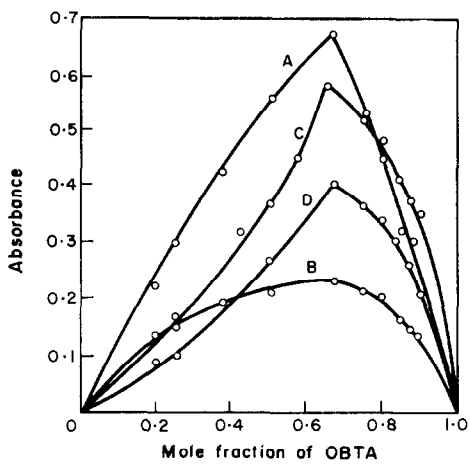


FIG. 5.—Job's curves for Rh(III)–OBTA system. Curves *A* and *B* are at pH 5·0 and wavelength 410 mμ; *C* and *D* at pH 12·0 and wavelength 475 mμ. Total concentration of Rh(III) and OBTA for curves *A* and *C* is $3{\cdot}07 \times 10^{-4}M$ and for *B* and *D* $1{\cdot}53 \times 10^{-4}M$.

The absorbance at 520 mμ due to the reagent is negligible, but that due to metal solution being significant, the function y, defined as the difference between the absorbance observed for a given mixture of metal and reagent after they have reacted, and the corresponding absorbance of the respective constituents for no reaction, was plotted against the mole fraction of the reagent (Fig. 4). The metal:ligand was found to be 1:3. The molar composition of the complex was also verified by the slope-ratio method of Harvey and Manning,[17] the ratio of the slopes of the straight line portions of the curves *A* and *B* (Fig. 6) being 2·8.

In order to determine the nature of the charge on the purple-violet complex, an aqueous ethanolic solution of the complex was passed through columns containing

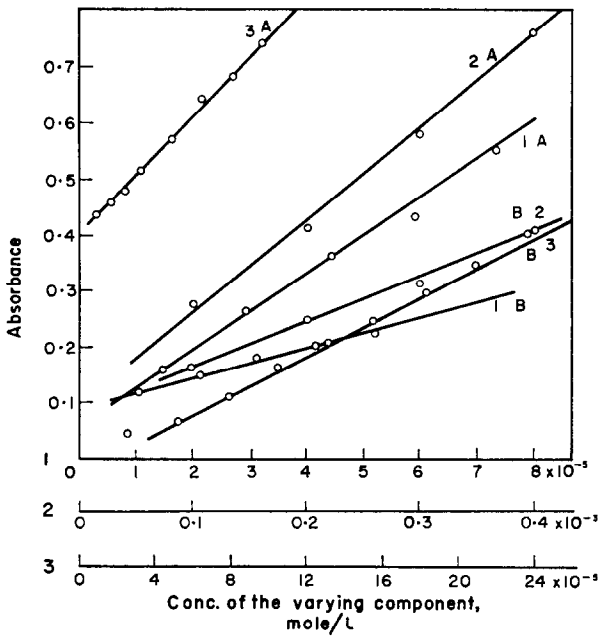
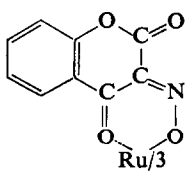


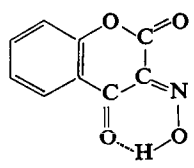
FIG. 6.—Slope-ratio method for composition of Ru and Rh complexes with OBTA. *1.* Ru(III)–OBTA complex, pH 3·5, $\lambda = 520$ mμ; *2.* Rh(III)–OBTA complex, pH 5·0, $\lambda = 410$ mμ; *3.* Rh(III)–OBTA complex, pH 12, $\lambda = 475$ mμ. In all cases, *A* corresponds to variation of metal concentration and *B* to variation of OBTA concentration.

Amberlite ion-exchange resins IRA-401(OH) (B.D.H.) and Ionenaustaucher-I (Merck's cation-exchange resin). It was observed that the complex was not exchanged by either of the two ion-exchangers, thus showing the neutral character of the complex.

Based on these facts, the tentative structure of the complex may be put down as (I), derived from the structure (II) for the reagent, given earlier by Bhat and Jain.[10]



(I)



(II)

The compositions of the two Rh–OBTA complexes were determined by the method of continuous variation at pH 5·0, $\lambda = 410$ mμ and at pH 12·0, $\lambda = 475$ mμ. For both the complexes, the metal:ligand ratio was found to be 1:2 (Fig. 5). This composition was confirmed by the slope-ratio method[17] at these wavelengths (Fig. 6).

The composition of the complex formed at lower pH was confirmed by gravimetry. Assuming a $1:n$ composition of the complex, the reaction can be written as:

$$RhCl_6^{3-} + nHL \rightarrow RhCl_{6-2n}L_n^{-(3-n)} + 2nCl^- + nH^+$$

where HL represents the ligand. The amount of chloride ions liberated was determined gravimetrically as silver chloride. An average of 4 Cl^- ions was found to be liberated per atom of rhodium.

The nature of the charge on the complex was determined by ion-exchange. It was observed that both the yellow-brown and the red brown complexes are completely exchanged by the anion-exchanger and not by the cation-exchanger, so the complexes are anionic.

Recommended procedure for the determination of rhodium(III) and ruthenium(III)

To 5 ml of solution containing 5–40 ppm of ruthenium(III) and/or 3–35 ppm of rhodium(III), add a tenfold excess of reagent solution in ethanol and heat in a boiling water-bath for 25 min if only ruthenium(III) is present, and for 45 min if rhodium is also to be determined. Cool, dilute to a known volume (10–25 ml) after bringing the pH to 1·5–5·0, and measure the absorbance against a reagent blank at 520 mμ to determine ruthenium. If rhodium is also present, measure the absorbance at 475 mμ as well; raise the pH to about 12·0 and again measure the absorbance at 475 mμ. The difference in absorbance at 475 mμ is due to rhodium(III). If only rhodium is present, then after heating for 45 min, cool, raise the pH to nearly 12, dilute to known volume (10–25 ml) and measure the absorbance at 475 mμ against a corresponding reagent blank.

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Zusammenfassung—Ruthenium(III) und Rhodium(III) bilden in äthanolischer Lösung mit Oximidobenzotetronsäure (OBTA) stabile farbige Komplexe. Ruthenium bildet einen purpurvioletten $Ru(OBTA)_3$-Komplex bei pH 1,1–3,5, der im pH-Bereich 1,1–11,3 stabil ist. Rhodium(III) bildet einen gelblichbraunen Komplex $RhCl_3(OBTA)_2$ bei pH 2–8; bei höherem pH (über 11,5) ist der Komplex rötlichbraun, zeigt aber dasselbe Verhältnis Rh: OBTA. Eine Methode zur gleichzeitigen Bestimmung dieser zwei Metalle wird vorgeschlagen; die Störungen durch häufig vorkommende Ionen wurden untersucht.

Résumé—Le ruthénium (III) et le rhodium (III) forment des complexes colorés stables en solution éthanolique avec l'acide oximidobenzotétronique (OBTA). Le ruthénium forme un complexe pourpre-violet $Ru(OBTA)_3$ à pH 1,1–3,5, qui est stable entre pH 1,1 et 11,3. Le rhodium (III) forme un complexe brun jaunâtre, $RhCl_3(OBTA)_2$, à pH 2–8; aux pH plus élèves (11,5 et au-dessus) le complexe est brun rougeâtre, mais a le même rapport Rh:OBTA. On propose une méthode pour le dosage simultané de ces deux métaux, et l'on a étudié les interférences des ions communément présents.

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SPECTROPHOTOMETRIC INVESTIGATION OF ASCORBINATE COMPLEXES OF METALS

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Summary—It has been shown that ascorbic acid forms metal complexes of the types ML and MHL, depending on the pH used, and that the complexes are relatively unstable, especially those of type MHL. Their absorption spectra have no maxima but have a steep slope at 320–380 mμ and are displaced to longer wavelengths relative to the absorption spectrum of ascorbic acid. A bigger shift occurs for elements of variable valency, and the spectra move to longer wavelengths as the pH is raised; at pH 7–9 a new maximum appears at 380–420 mμ, indicating a change of structure of the ascorbinate ion, probably with a lactone. Metals can be determined spectrophotometrically as their ascorbinates, at concentrations down to $10^{-5}M$ for Ti, U, Os, V, Cr, Nb, Ta, Zr, Mo, W, Sn, Pb and Th, and $10^{-4}M$ for lanthanides, Sc, Hf and Sb.

ALTHOUGH ascorbic acid is well-known as a reductant, there are only scattered references in the literature to its use as a complexing agent, mainly for the yellow complexes formed by titanium and uranium. We have made a thorough spectrophotometric study of the ascorbinate complexes of metals in most groups of the periodic table. The alkali metals were not investigated because the spectrophotometric method was not applicable, and no investigation was made of systems in which ascorbic acid was known to act as a reductant.

EXPERIMENTAL

l-Ascorbic acid[1] is 2,3-endiol-*l*-gulono-1,4-lactone. The value of pK_1, for the 3-hydroxy group, is 4·2, and pK_2, for the 2-hydroxy group, is 11·6. The reducing properties are due to the grouping —C(OH)=C(OH)—C=O with two conjugated double bonds, and the complexing properties arise from the 2,3-endiol configuration. Both properties sometimes operate simultaneously. The absorption spectrum of ascorbic acid shows a maximum at 245 mμ in acidic media and at 265 mμ in alkaline media. Ascorbic acid should not be used as a complexing agent at very high pH (where it will undergo hydrolytic and oxidative reactions).

Reagents and apparatus

Freshly prepared solutions of ascorbic acid were used throughout, and stabilizers, which might have interfered with the study of complex formation, were omitted. Any buffering action needed was supplied by the reagent and its salts. A large excess of reagent was added to make complex formation as complete as possible. Spectra were recorded on SF-4 and SF-5 spectrophotometers against a reagent blank. A pH meter and glass electrode were used for pH measurements. Because of the strong absorption of light below 300–320 mμ by ascorbic acid, the reagent could be used as a compensatory blank only at wavelengths longer than this, and 320 mμ was taken as the lower boundary for absorption spectra. Solutions of the metal chlorides were generally used.

Absorption spectra of the complexes

Absorption spectra were recorded for the ascorbinate complexes of the elements listed in Tables I and II and for thallium(I), ytterbium, germanium, arsenic, antimony, selenium, tellurium, rhenium and platinum(II). The general features were that the spectra of simple salts showed an increase in absorbance in the 320–380 mμ region, or a displacement to longer wavelengths in the presence of ascorbic acid (Table I). As the pH was increased the absorption bands shifted to longer wavelengths,

TABLE I.—THE MAJOR CHANGES IN ABSORPTION SPECTRA WHEN ASCORBINATE COMPLEXES ARE FORMED

Element	Absorption maximum of pure salt		Absorption maximum in 0·5*M* ascorbic acid		pH
	λ_{max}, mμ	ε	λ_{max}, mμ	ε	
Pr	480	1·15	485	3·10	4·5
Nd	520	1·75	525	3·75	4·5
	575	6·00	580	12·0	
	740	2·80	745	6·00	
	790	2·00	800	8·00	
	870	0·90	870	2·25	
Sm	400	2·15	405	7·40*	4·5
Dy	365	1·45	365	2·45*	4·5
	390	0·50	390	1·70*	
Ho	360	1·60	360	5·75	4·5
	415–420	1·00	420	2·20	
	450	2·95	450	12·6	<
	540	2·35	540	3·65	
Er	380	1·85	380	9·80	
	520	1·45	525	7·15	
Cr(III)	580	18·5	600	80	5·0
W			660	800	11·0
Fe(II)			500	1950	9·0
Co(II)	500	4	540	55	8·0
Ni	400	5	400	94	8·0
Os			420	1600	3·5

* Peak affected by high absorbance of reagent in the ultraviolet region.

and then above a certain critical pH the reverse shift occurred. If measurements were made at a single wavelength, then the pH producing maximum absorbance varied with the electrovalency of the ion. For tervalent elements it was 5·5, for quadrivalent 4·5–5·5, for quinquevalent 4·0 and for sexivalent 3·5. The reason for this is the effect of the charge on the metal ion on the pH at which hydrolysis begins.

The molar absorptivities at 320, 330 and 380 mμ and the pH of maximum absorbance were calculated in order to provide a comparison of the sensitivity available in spectrophotometric determination of metals as ascorbinates, and are shown in Fig. 1.

The biggest spectral shift was observed with highly charged ions which are capable of reduction to a lower oxidation state. This does not mean that they are reduced by ascorbic acid, but rather that the reducing properties of ascorbic acid are manifested in charge transfer complex formation. For example, the molar absorptivity of the titanium complex (7000 at 380 mμ) is much greater than that of zirconium (100) or hafnium (50) at the same wavelength. Similarly that for niobium (1100) is higher than that for tantalum (250), and europium (which can form Eu^{2+}) gives the highest value for the lanthanide complexes. The determination of europium in mixtures of lanthanides by this method seems very promising, the only serious interference coming from lutetium.

The spectra of the complexes of bivalent ions (Mg, Ca, Sr, Ba, Zn, Cd, Sn, Pb, Mn, Co, Ni and Fe) have a maximum at 380–420 mμ and pH 7–9 (Table II). Tervalent ions do not show this maximum, with the exception of europium and samarium, which may be reduced to the bivalent state by the reagent. For Ti, Zr, Nb and U this maximum does not stand out against the general background of intense absorption.

The ascorbinate complexes of metals with variable valences and maximum oxidation states ranging from III to VI [Eu, Ho, Er, Zr, Hf, Nb, Ta, V(IV), Mo and W] were examined in more detail, the composition, instability constants and molar absorptivities being obtained.

RESULTS AND DISCUSSION

Calculation of constants for the complexes

We assumed that metal ions and ascorbic acid reacted to form complexes of the type $M(HA)_n$ and MA_n where HA and A are the singly and doubly dissociated ions

TABLE II.—ABSORPTIVITIES OF ASCORBINATE COMPLEXES AT pH9 IN 0·5*M* ASCORBIC ACID, MEASURED AGAINST 0·5*M* ASCORBIC ACID

Element	ϵ	λ_{max}, $m\mu$
Be	hydrolyses	390
Mg	39	390
Ca	37	400
Sr	9	400
Ba	6	400
Zn	8	400
Cd	41	380
B	0	390–400
Al	1	395
Ga	−4	390
In	1·5	400
Sc	3	420
Y	9·5	410
la	16·5	390
Th	hydrolyses	
U	2700	390
Sn(II)	22·5	390
Sn(IV)	−135	390
Pb	330	390
Ti	3200	400
Zr	165	400
Hf	20	400
Bi	620	390
V	—10	390
Nb	465	390
Ta	—160	400
Cr(III)	150	380
Mo	125	390
W	−60	390
Mn	560	390
Fe(II)	1325	380
Co(II)	215	390
Ni	800	390
Ce	14	390
Pr	10·3	390
Nd	45	390
Sm	6	390
Eu	1625	390
Gd	5·5	390
Tb	−5·5	390
Dy	−3·0	390
Ho	1·5	390
Er	−5·0	390
Lu	300	390

of ascorbic acid, charges being omitted for the sake of simplicity. We further supposed that in defined conditions only one product exists, *i.e.*,

$$M^{z+} + nH_2A \rightleftharpoons [M(H_mA)_n]^{[z-(2-m)n]+} + (2-m)nH^+. \quad (1)$$

Then the equilibrium constant, K, is given quite generally by

$$K = \frac{[M(H_mA)_n][H]^{n(2-m)}}{[M][H_2A]^n} \quad (2)$$

where m is 0 or 1. This equation gives the ratio of the concentrations of the complex

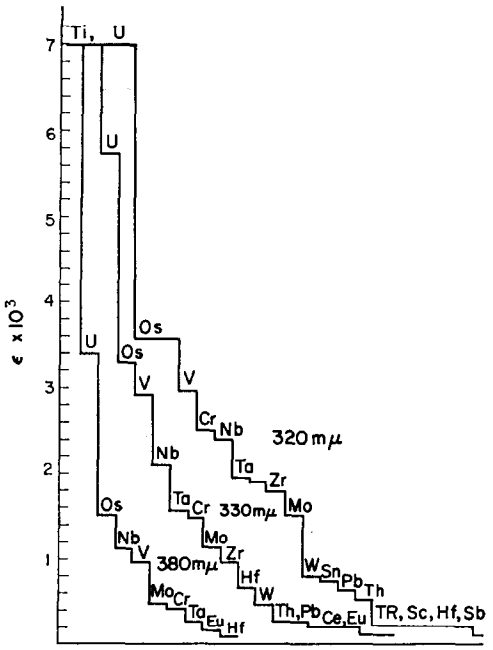

FIG. 1.—Molar absorptivities of ascorbinate complexes at wavelengths shown.

and the free metal ion. If the dissociation constant pK_1 for the first dissociation of ascorbic acid is taken into account together with the relationship of the absorbance, A, of the solution to the concentration of the complex, then

$$A = \varepsilon d[M(H_mA)_n] \tag{3}$$

where ε is the molar absorptivity of the complex and d is the length of the light-path in the cuvette, and we have

$$\frac{[M(H_mA)_n]}{[M]} = K' \frac{[HA]^n}{[H]^{n(1-m)}} = \frac{A}{\varepsilon d(C_M - A/\varepsilon d)} \tag{4}$$

where C_M is the total concentration of all the metal species, and $K' = K/K_1^n$.

If a maximum occurs in a plot of absorbance *vs.* ligand concentration it is a simple matter to calculate ε and the other quantities, but if no maximum appears then we use the expression

$$\frac{1}{E} = \frac{1}{C_M\varepsilon} + \frac{[H]^{n(1-m)}}{C_M\varepsilon K'[HA]^n} \tag{5}$$

where E, the extinction modulus, is given by A/d. Sommer used a similar expression in his investigation of the ascorbinate complexes of titanium.[2]

From this equation it follows that for complexes of the type $M(HA)_n$ the magnitude of $1/E$, and hence of A, is independent of pH if the ligand concentration is constant, but that for MA_n complexes there will be a pH-dependence. For a particular value of n (and at constant pH in the case of MA_n complexes) a plot of $1/E = f(1/[HA]^n)$ will yield a straight line with an intercept at $1/C_M\varepsilon$ on the y axis, from which ε can be determined. The slope of the line will be $1/C_M\varepsilon K'$, and K' can be

determined from it, and hence the instability constant K_{mn} of the complex can be calculated.

$$K_{mn} = \frac{[M][H_mA]^n}{[M(H_mA)_n]} = \frac{[H]^{n(1-m)}[H_mA]^n}{K'[HA]^n}. \quad (6)$$

For $m = 1$, $K_{1n} = 1/K'$ or $pK_{1n} = \log K'$, and for $m = 0$, $K_{0n} = K_2^n/K'$ or $pK_{0n} = npK_2 + \log K'$, where K_2 is the second dissociation constant for ascorbic acid.

The concentration of HA was calculated from the total ascorbic acid concentration, C_{H_2A}, and the pH, taking into account the degree of dissociation[3] of the sodium ascorbinate produced in adjusting the pH. This was done on the basis of the equations

$$C_{H_2A} = [H_2A] + [HA] + [NaHA] \quad (7)$$

$$K_1 = [H][HA]/[H_2A] = 10^{-4\cdot2} \quad (8)$$

$$K_{NaHA} = \frac{[Na][HA]}{[NaHA]} \sim 1\cdot5 \times 10^{-2} \quad (9)$$

$$C_{Na} = [Na] + [NaHA] \quad (10)$$

$$[HA] = \left\{\left[\frac{K_{NaHA} + C_{Na} - C_{H_2A} + [H]K_{NaHA}/K_1}{2(1 + [H]/K_1)}\right]^2 + \frac{C_{H_2A}K_{NaHA}}{1 + [H]/K_1}\right\}^{1/2} - \frac{K_{NaHA} + C_{Na} - C_{H_2A} + [H]K_{NaHA}/K_1}{2(1 + [H]/K_1)}. \quad (11)$$

It should be noted that the HA concentration will be maximal at pH 4·2, the half-neutralization point.

Plots were made for a fixed total concentration of metal and several different concentrations of ascorbic acid, as shown in Fig. 2 for neodymium. The absorbances were measured at the appropriate wavelength of maximum absorption (580, 380, 450 and 378 mμ for Nd, Eu, Ho and Er respectively) or on the short-wave side of an

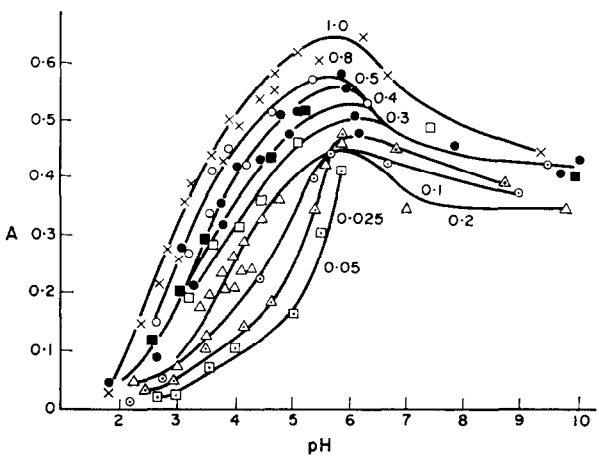

FIG. 2.—Variation in absorbance at 583 mμ of 0·0084M neodymium as a function of pH, in 0·025–1·00M ascorbic acid.

absorption peak (at 330 mμ for Zr, Hf, Nb, Ta, V, Mo and W). Plots of absorbance *vs.* concentration of HA were then made for each pH, as shown for neodymium in Fig. 3.

The results show that complexes of the type $M(HA)_n$ are formed at pH 2–4 with tervalent metals, 0–1 with quadrivalent metals, 0–0·5 with quinquevalent, and less than 0 with sexivalent metals. The pH of formation of this type of complex decreases with increase in the formal charge on the ion and is lower for the lower members of a particular group in the periodic classification.

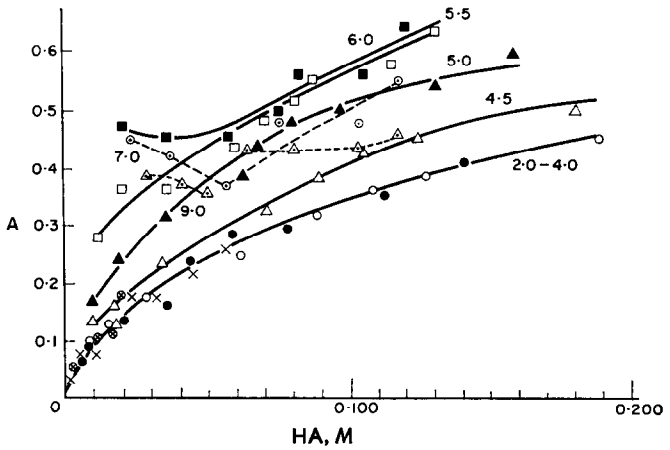

FIG. 3.—Variation in absorbance at 583 mμ of 0·0084*M* neodymium as a function of ascorbic acid concentration, at pH 2–9.

Complexes of the type MA_n are formed with tervalent metals at pH values above 4, but above pH 6 hydrolysis of the metal ion begins, especially if the concentration of ascorbic acid is low . For ions of oxidation state greater than IV, MA_n complexes are formed at pH values ranging up to 4 from the upper limit for formation of $M(HA)_n$ complexes, and hydrolysis sets in above this level.

The plots of $1/E$ *vs.* $f(1/[HA]^n)$ all gave values of unity for n, showing that all the complexes are either MA or MHA. The values calculated for the molar absorptivities and the instability constants are shown in Table III. Some of the instability constants were calculated for pH 2·5–4·0 from the relationship

$$K_{mn} = \frac{C'C''(A'' - A')}{A'C'' - A''C'} \tag{12}$$

where A' and A'' are the absorbances for a fixed concentration of metal and concentrations C' and C'' of ligand, and are given in Table IV. The ionic strength in the systems examined was varied from 0·1 to 0·3.

It is evident from the results that the stability of the complexes increases with the oxidation number of the metal ion, *e.g.*, Nb > Zr > Y, and with increasing atomic number within a group, *e.g.*, Hf > Zr > Ti (3.1[2]).

Considerably fewer facts are available about the MA_n complexes, but they are much more stable than the $M(HA)_n$ complexes, and are much more useful analytically,

TABLE III.—INSTABILITY CONSTANTS AND MOLAR ABSORPTIVITIES OF MHA ASCORBINATE COMPLEXES

Element	λ_{max}, $m\mu$	MHA					
		pH	pK_{11}	ε_{11}	pH	pK_{01}	ε_{01}
Nd	582–583	2·0–4·0	1·2	18	6·0	6·8	2·7
Eu	380	3·0–4·0	0·8	300			
Ho	451	2·0–4·0	1·0	22	6·0	6·4	112
Er	378	2·0–4·0	0·5	47	6·0	5·9	314
Zr	330	0·0–1·0	3·2	400	4·0	9·5	1040
Hf	330	0·0–0·5	4·2	65	4·0	8·0	500
V(IV)	330	2·0–4·0	1·8	1500	5·0	7·1	7800
Nb	330	0·0–0·5	5·5	350	4·0	9·4	2300
Ta	330	0·0	5·0	870	4·0	9·5	1700
Mo	330	0·0	4·6	1250			

TABLE IV.—INSTABILITY CONSTANTS FOR MHA ASCORBINATE COMPLEXES OF RARE EARTHS, SCANDIUM AND YTTRIUM

Element	pK	Element	pK
Sc	1·3	Gd	0·1
Y	1·8	Tb	1·3
La	2·5	Dy	0·6
Ce	0.9	Yt	1·1
Pr	0·8	Lu	1·3
Sa	1·2		

in terms of the colour developed. In no case has a complex been obtained containing more than one ascorbinate group per metal ion. The occurrence of negatively charged ascorbinates of zirconium, vanadium, molybdenum and tungsten[4] may be ascribed to addition of hydroxyl groups, as for instance in the uranyl compound[5] $[UO_2(C_6H_7)_6(OH)_2]^{-}$.

It was found that vanadium(IV) was reduced to vanadium(III) by ascorbic acid as well as being complexed. Similar effects were observed with tungsten and the MA complex of molybdenum, and it was impossible to obtain any quantitative information about these systems. The optimum conditions for reduction of tungsten were to start at pH 1·6 and end at pH 11·0. The colour was stable for at least an hour, and the absorption maximum was at 760 mμ for pH 5·5–5·9, shifting to 660 mμ for alkaline conditions. A 100-fold molar excess of ascorbic acid gave the best results.

The complexes formed in alkaline media were kinetically unstable. The absorbance obtained depends on the temperature, degree of exposure to light, and the rate of mixing of the solutions. Adjustment of the pH also presents problems, since addition of buffer causes a sharp decrease in the absorbance. The reagent is not self-buffering in the alkaline region.

When the europium system was examined more closely it was found that EuHA is formed at pH 3·0–4·5, with $\varepsilon_{380} = 300$ and $pK_{11} = 0{\cdot}8$. At pH values above 5 the

absorption maximum increases with pH and shifts to longer wavelengths, reaching a maximum absorbance at pH 9 and 390 mμ. Some evidence was found that the complex Eu_2A is formed at this pH (molar absorptivity 3250). It seems likely that the lactone ring of ascorbic acid is broken in forming this complex.

Quantitative applications

It was found that Beer's law was obeyed over the metal ion concentration range 10^{-3}–$10^{-4}M$. Spectrophotometric determinations in the visible region can be made with a limiting lower concentration of $10^{-5}M$ for osmium (420 mμ), iron(II) (500 mμ), and tungsten (660 mμ), $10^{-4}M$ for chromium(III) (600 mμ), and $10^{-3}M$ for holmium (450 mμ), cobalt (540 mμ) and neodymium (575 mμ).

The instability constants reported are regarded by us as tentative since no allowance is made in the calculations for hydrolysis or reduction reactions. Some applications of the reagent have been reported elsewhere.[6–9]

Zusammenfassung—Es wurde gezeigt, daß Ascorbinsäure je nach pH Metallkomplexe der Typen ML und MHL bildet und daß die Komplexe, besonders die vom MHL-Typ, relativ instabil sind. Ihre Absorptionsspektren haben keine Maxima, sondern einen steilen Anstieg bei 320–380 nm und sind relativz um Absorptionsspektrum der Ascorbinsäure langwellit verschoben. Die Verschiebung ist gröber bei Elementen von variabler Wertigkeit; die Spektren wandern bei steigendem pH zu längeren Wellen. Bei pH 7–9 erscheint ein neues Maximum bei 380–420 nm, das auf eine Strukturänderung im Ascorbinat-Ion deutet, möglicherweise zu einem Lacton. Metalle konnen als Ascorbinate spektrophotometrisch bestimmt werden, Ti, U, Os, V, Cr, Nb, Ta, Zr, Mo, W, Sn, Pb und Th bei Konzentrationen bis herunter zu 10^{-5}M, Lanthaniden, Sc, Hf und Sb bis 10^{-4}M.

Résumé—On a montré que l'acide ascorbique forme des complexes métalliques des types ML et MHL, selon le pH utilisé, et que le complexes sont relativement instables, particulièrement ceux du type MHL. Leurs spectres d'absorption n'ont pas de maximum mais ont une pente très marquées à 320–380 mμ et sont déplacés vers les plus grandes longueurs d'onde par rapport au spectre d'absorption de l'acide ascorbique. Un plus grand déplacement se produit avec les éléments de valence variable, et les spectres se déplacent vers les plus grandes longeurs d'onde lorsqu'on élève le pH; à pH 7–9, il apparaît un nouveau maximum à 380–420 mμ indiquant un changement de structure de l'ion ascorbinate, probablement en une lactone. On peut doser spectrophotométriquement les métaux à l'état d'ascorbinates, à des concentrations descendant jusqu'à 10^{-5} *M* pour Ti, U, Os, V, Cr, Nb, Ta, Zr, Mo, W, Sn, Pb et Th et 10^{-4} *M* pour les lanthanides, Sc, Hf et Sb.

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REDOX REACTIONS ON COLUMNS

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Summary—In a study of redox reactions on columns, the work of Cerrai and Testa has been extended. It has been shown that insolubility of the redox compound is the most important factor and that adsorptive forces play little or no part. A useful redox column method for the determination of iron and vanadium, which compares favourably with that using a Jones reductor column, has been developed. The redox potentials of several substituted hydroquinones have been measured.

METAL reductor columns have been used widely since the last century, but it is well-known that they are not completely satisfactory for all purposes. For example, there is still some uncertainty about the formation of hydrogen peroxide and the literature contains many conflicting statements.[1] In our own experience hydrogen peroxide is always formed with all types of metal reductor unless atmospheric oxygen is rigorously excluded from the system.[2]

As long ago as 1949, Cassidy[3] prepared "redox" or electron-exchange polymers consisting of vinyl polymers with pendant dihydroxyphenyl groups. Although the results obtained on columns packed with these polymers were promising, little attempt has been made to apply the technique. This may be due to the slow reactions and the comparative chemical instability of many of the products. Several reviews have been published on this topic and other types of electron-exchangers have also been described.[4]

Cerrai and Testa[5] recognized these shortcomings and attempted to prepare simpler systems; "the desired characteristics were that the organic solutions (of a simple redox compound) should be absorbed by the porous support in such a way that the redox molecules would be stably fixed to the surface and ready to react". Cerrai and Testa finally recommended columns packed with tetrachlorohydroquinone supported on Kel-F powder (polytrifluorochloroethylene).

The results obtained with these columns were very promising; Cerrai and Testa were able to effect redox reactions with a variety of compounds and of especial value was the use of the "memory" of the column, which enabled indirect determinations to be made, so preserving the uncontaminated effluent for other purposes.

It is not altogether clear from Cerrai and Testa's paper, whether the system depends entirely on water-insolubility or that weak adsorptive forces are involved; Betteridge[4] certainly considers that the latter play some part. A considerable amount of further experimentation is also necessary to establish the life of the columns after extended usage; comparison of the determinations against well-established methods and determinations at varying levels are also required. There is also the possibility that the same principle might be used for chelating systems. The present paper describes further studies on these factors. Other substrates and compounds having

redox properties have been examined; the formal potentials of the compounds have been determined.

EXPERIMENTAL

Materials

Polytrifluorochloroethylene	Kel-F, KF 6069, Minnesota Mining & Manufacturing Company.
Polytetrafluoroethylene	Grade 4 I.C.I. Ltd.
Polyethylene	Grade 617A Kingsley & Keith (Chemicals) Ltd.
Polystyrene	Monsanto Ltd.
Polyacrylonitrile	Masslinn 200 Schweitzer Division, Kimberly-Clark Corporation.
Polyvinyl Chloride	VY 19 Bakelite Xylonite Ltd.
Kieselguhr	B.D.H. Ltd.
Celite A	80–120 mesh B.D.H. Ltd.
Tetrachlorohydroquinone	Eastman Organic Chemicals; (Kodak Ltd.)
Tetrafluorohydroquinone	H.F.A. 61 Imperial Smelting
Anthraquinone	Hopkin & Williams Ltd.
p-Aminophenol	B.D.H. Ltd.
t-Butyl catechol	Dr. J. R. Majer (Birmingham University)
Alloxan	B.D.H. Ltd.
1:10 Phenanthroline monohydrate	The G. Frederick Smith Chemical Co., Columbus, Ohio.

Preparation of redox columns

The Kel-F powder was passed through a 14-mesh sieve to remove the larger particles. It was then coated with 30% w/w tetrachlorohydroquinone according to the method of Cerrai and Testa[5] by evaporating the solvent from the slurry of the powder and an ether solution of the tetrachlorohydroquinone. The resulting powder was made into a smooth paste with dilute hydrochloric acid and poured into a 1-cm diameter glass column fitted with a sintered disc and tap.

Determination of permanence of columns

Columns (8 cm long) were alternately completely oxidized and reduced by passage of an excess of oxidant or reductant solution, the column capacity being measured by back-titration of the eluate. The oxidant solution was 0·1*M* iron(III) chloride in 0·03*M* hydrochloric acid. Three reductant solutions were used: 0·1*M* iron(II) sulphate in 8*M* hydrochloric acid, 0·1*N* tin(II) chloride in 2*M* hydrochloric acid and 0·1*N* ascorbic acid in water. Of these three solutions, the ascorbic acid was the most stable.

Reduction of ferric chloride solution

A column (21 cm long) of 10 g of coated Kel-F powder was washed with 0·3*M* hydrochloric acid and 25 ml of iron(III) chloride solution in 0·03*M* hydrochloric acid were allowed to pass through the column during 1 hr. The column was then washed with 50 ml of 0·03*M* hydrochloric acid and the combined eluate was titrated with 0·1*N* potassium dichromate in the presence of phosphoric acid, diphenylamine being used as indicator.

Portions of the same iron(III) chloride solution were standardized volumetrically by reduction with sulphur dioxide and titration with cerium(IV) sulphate.

Reduction of ammonium vanadate solution

A column containing 5 g of 20% w/w tetrachlorohydroquinone on Kel-F powder was washed with 1*M* sulphuric acid, and 25 ml of ammonium vanadate solution in 1*M* sulphuric acid were passed through. The column was then washed with 25 ml of water and the combined eluate titrated with 0·1*M* potassium permanganate.

The amount of tetrachloroquinone produced on the column was determined by passing 25 ml of 0·2*N* ascorbic acid through the column, washing with 25 ml of water, and titrating the combined eluate with standard iodine solution. Portions of the same ammonium vanadate solution were also standardized by reduction with sulphur dioxide followed by titration with standard potassium permanganate solution.

Liquid electron-exchange systems

Portions (10 or 25 ml) of 0·100*M* iron(III) chloride in 0·3*M* hydrochloric acid were shaken with a solution of 0·5 g of tetrachlorohydroquinone in 50 ml of organic solvent (xylene–lauryl alcohol 90:10). Shaking times of 5–30 min were used. The aqueous layer was run off and the organic layer extracted with two 10-ml lots of water for 1 min each. The three aqueous layers were combined and titrated with 0·1*N* potassium dichromate. The partially-oxidized tetrachlorohydroquinone solution was reduced with excess of ascorbic acid solution, and 0·1*N* iodine was used to determine the amount of unreacted ascorbic acid.

Formal redox potential measurements

A 50-ml portion of a solution of the redox compound and hydrochloric acid in water or an ethanol-water mixture was placed in a 100-ml beaker, and stirred by a magnetic stirrer. A platinum foil electrode and a saturated calomel electrode in conjunction with a Pye pH meter were used to measure the potential. The oxidizing or reducing solution was added in small amounts at a time from a burette. To match the column conditions as closely as possible, an inert atmosphere was not used.

The point at which the redox compound had reacted completely was denoted by a rapid increase or decrease in potential for a small addition of titrant. This was preceded by a relatively flat portion of the potential–volume curve, the point of inflexion of which gave the formal redox potential, *i.e.*, the potential at which the redox compound is half-oxidized and half-reduced.

RESULTS AND DISCUSSION

Organic polymers such as polytetrafluoroethylene (PTFE), polyethylene, polyvinyl chloride and polyacrylonitrile retained tetrachlorohydroquinone to the same extent as Kel-F, no polymer possessing any markedly better retentive properties. Polystyrene presented preparative difficulties because it was soluble in the solvents used to deposit the tetrachlorohydroquinone. The permanence of such columns was checked by submitting two PTFE and two Kel-F columns to nine successive oxidation-reduction cycles each. After an initial 4–10% loss in capacity, all of the four columns settled down to a loss of only 0·1–1·2% per oxidation or reduction stage, compared with the 2% obtained by Cerrai and Testa.[6]

The permanence of the tetrachlorohydroquinone so obtained prompted an investigation of other reactants for use on columns. Alternative redox agents examined were alloxan, anthraquinone, t-butylcatechol, *p*-aminophenol, vanadium(II) 1,10-phenanthrolinate[7] and iron(II) 1,10-phenanthrolinate. In no case, except with anthraquinone, was the redox compound retained on the columns. Anthraquinone, which is water-insoluble like the other compounds reported by Cerrai and Testa,[5] was retained, but its standard redox potential[8] of 0·15 V is so low that the number of systems that could be oxidized by it is very limited.

Chelation reactions of nickel and cobalt with dimethylglyoxime and α-benzildioxime were studied on columns. Chelation was rapid with the former reagent, but the chelate was washed from the column. The second reagent, though more insoluble, reacted too slowly to be useful.

These redox and chelation results suggested that the reason for reasonable permanence on a column is that the compound is insoluble in the solvents, usually water, passed through the column. The alternatives are that there is adsorption due to a chemisorptive effect or to van der Waals forces. To eliminate these latter possibilities, the behaviour of other types of substrate with tetrachlorohydroquinone was

studied and also redox compounds of similar chemical structure but of greater solubility were used.

Inorganic substrates such as kieselguhr and diatomaceous earth (Celite) behaved as well as organic polymers in giving columns of satisfactory permanence, the capacity losses per oxidation or reduction step being 0·2–0·35%.

Tetrafluorohydroquinone and hydroquinone were tested as redox compounds that were water-soluble and of similar chemical structure to tetrachlorohydroquinone. However, they were not retained by columns of either inorganic or organic substrates. Especially in the case of tetrafluorohydroquinone does this point towards the insolubility effect being the all-important factor. The tetrafluorohydroquinone and tetrachlorohydroquinone are as chemically alike as is possible, so that any chemical bonding to the substrate should be just as probable with one as with the other. The outstanding difference between them is in their water-solubilities and it was therefore concluded that the tetrachlorohydroquinone remains on the column because of its insolubility. The substrate serves to hold the redox compound in a finely-divided state and so increases its efficiency.

The practical possibilities of using a redox column as a laboratory tool were evaluated. Blank runs, in which solvents only were passed through the columns gave very small or negligible corrections, equivalent to a loss per cycle of only 0·2% of the column capacity. Through-put rates could be increased from 30 ml/hr for a 1-cm diameter column to 180 ml/hr for a 3-cm diameter column, and still allow complete reaction of the material passed through the column.

The accuracy of the determination of solutions of iron(III) chloride in 0·03*M* hydrochloric acid was checked by comparison with reduction by sulphur dioxide followed by titration with cerium(IV) sulphate. The results are presented in Table I, and it can be seen that agreement is excellent.

A similar comparison was made for the reduction of ammonium vanadate solution by the column and by sulphur dioxide. In each case the reduced solution was titrated with standard potassium permanganate solution. It was also possible to make a further measurement of the amount of ammonium vanadate reduced, by determining the amount of tetrachlorohydroquinone oxidized on the column. This was achieved by passing a standard solution of ascorbic acid through the column and titrating the effluent with standard iodine solution. The results of this comparison are given in Table II, and it can be seen that there is agreement between results obtained by column and by sulphur dioxide reduction, but that results using the column "memory"

TABLE I.—DETERMINATION OF IRON(III) CHLORIDE SOLUTION IN 0·03*M* HYDROCHLORIC ACID SOLUTION

Method	Iron(III), *M*
Column reduction, potassium dichromate titration	0·0994 0·0994 0·0994
Sulphur dioxide reduction, ceric sulphate titration	0·0996 0·0996 0·0996

TABLE II.—STRENGTH OF AMMONIUM VANADATE SOLUTION IN 1*M* SULPHURIC ACID

Method	Vanadate, *M*	Mean, *M*
Column reduction, potassium permanganate titration	0·1019 0·1042 0·1042 0·1042 0·1042 0·1042	0·1038
Column reduction, ascorbic acid titration	0·1036 0·1036 0·1010 0·1028 0·1019 0·1036 0·1019 0·1028	0·1027
Sulphur dioxide reduction, potassium permanganate titration	0·1035 0·1041 0·1035 0·1030	0·1035

are up to 1% low. Similar results were obtained with iron(III). These slightly low results may be due to tetrachloroquinone being slightly more soluble than the hydroquinone; possibly the effect could be overcome by incorporating a short section of untreated substrate at the bottom of the column.

The liquid electron-exchange systems described by Danesi *et al.* have been evaluated and found to offer no advantages over redox columns. They claimed that electron-exchange at a liquid-liquid interface between tetrachlorohydroquinone in an organic solvent and an aqueous solution of metal ions could be expected to be faster than on columns, because there would be no slow diffusion of the ions through the resin as the rate-determining step. However, the redox reaction is an equilibrium and the two-phase liquid method does not readily give a complete reaction, as shown in Tables III and IV. On the other hand, the use of a column pushes the reaction to completion, because the column product is left behind in the upper part and fresh reactant is presented to the test solution as it descends.

Formal redox potentials were measured for tetrachlorohydroquinone, tetrafluorohydroquinone and hydroquinone. Because of the insolubility of the first of these, ethanol–water mixtures were used as solvent. Conant and Fieser[10] have reported that potentials are not highly dependent upon the solvent and this is also demonstrated by the values obtained for hydroquinone (Table V). The results in

TABLE III.—DEPENDENCE OF EXTENT OF IRON(III) CHLORIDE REDUCTION ON QUANTITY USED AND SHAKING TIME

$[Fe^{3+}]/[TCHQ]$	Shaking time, *min*	Iron reduced, %
1:1·6	5	50·6
	20	82·6
	30	78·6
1:4	10	76·0
	20	95·0
	30	100·0

TABLE IV.—DEPENDENCE OF EXTENT OF ASCORBIC ACID OXIDATION ON SHAKING TIME

Shaking time, *min*	Ascorbic acid oxidized, %
10	72·0
20	84·3
30	97·5

TABLE V.—FORMAL REDOX POTENTIALS IN ETHANOL–WATER MIXTURES

Redox compound	Ethanol–water ratio in solvent	Formal redox potential,† *V*
HQ*	0:100	+0·59
HQ	50:50	+0·61
HQ	70:30	+0·60
TCHQ‡	50:50	+0·56
TCHQ	70:30	+0·57
TFHQ¶	0:100	+0·59

Oxidant—iron(III) chloride in 0·03*M* hydrochloric acid.
*HQ = Hydroquinone.
‡TCHQ = Tetrachlorohydroquinone.
¶TFHQ = Tetrafluorohydroquinone.
†IUPAC convention (*J. Am. Chem. Soc.*, 1960, **82**, 5517).

TABLE VI.—EFFECT OF ACIDITY ON FORMAL REDOX POTENTIALS MEASURED DURING OXIDATION OR REDUCTION

Redox compound	Ethanol–water ratio in solvent	[HCl], *M*	Oxidant	Reductant	Formal redox potential, *V*
HQ	70:30	0·03	$FeCl_3$	—	0·60
HQ	70:30	2	NH_4VO_3	—	0·70
Q*	70:30	2	—	$SnCl_2$	0·68
TCHQ	70:30	0·03	$FeCl_3$	—	0·57
TCHQ	70:30	2	NH_4VO_3	—	0·68
TCQ†	95:5	0·0	—	Ascorbic acid	0·50
TCQ	78:22	2	—	$SnCl_2$	0·71
TFHQ	0:100	0·0	$FeCl_3$	—	0·51
TFHQ	0:100	0·03	$FeCl_3$	—	0·59
TFHQ	0:100	2	NH_4VO_3	—	0·69
TFQ‡	0:100	0·03	—	Ascorbic acid	0·60
TFQ	0:100	2	—	$SnCl_2$	0·70

* Q = Quinone.
† TCQ = Tetrachloroquinone.
‡ TFQ = Tetrafluoroquinone.

Table V show that the presence of chlorine or fluorine as substituents in the nucleus has little effect on the value of the potential. The results in Table VI show that the redox potentials are dependent on the acidity. This is in agreement with the report of Cerrai and Testa[5] that iron(III) is reduced to iron(II) in 0·03*M* hydrochloric acid whereas in 8*M* hydrochloric acid, iron(II) is oxidized to iron(III) by tetrachloroquinone, though it must be remembered that the iron(II)/iron(III) couple has a potential dependent on the chloride concentration.

Conclusions

Redox or electron-exchange columns may be rapidly and simply prepared. They maintain their redox capacity effectively and have been shown to give reliable results in the determination of iron(III) and vanadium(V). However, it would be necessary to test them thoroughly in the presence of other metals and under routine conditions before they could replace metal reductor-columns for the determination of iron and vanadium.

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Zusammenfassung—In einer Untersuchung über Redoxreaktionen an Säulen wurde die Arbeit von Cerrai und Testa erweitert. Es wurde gezeigt, daß die Unlöslichkeit der Redoxverbindung der wichtigste Faktor ist und adsorptive Kräfte wenig oder keine Rolle spielen. Ein nützliches Säulenredoxverfahren zur Bestimmung von Eisen und Vanadium wurde entwickelt, das beim Vergleich mit einer Jones-Reduktorsäule gut abschneidet. Die Redoxpotentiale mehrerer substituierter Hydrochinone wurden gemessen.

Résumé—Dans une étude des réactions redox sur colonnes, on a développé le travail de Cerrai et Testa. On a montré que l'insolubilité du composé redox est le facteur le plus important et que les forces d'adsorption ne jouent qu'un rôle faible ou nul. On a élaboré une méthode de colonne redox utile pour le dosage du fer et du vanadium, qui est favorablement comparable à celle utilisant une colonne de réducteur de Jones. On a mesuré les potentiels redox de plusieurs hydroquinones substituées.

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INTERACTION OF DOWEX A-1 CHELATING RESIN WITH SPARINGLY SOLUBLE CALCIUM SALTS

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Summary—The interaction between Dowex A-1 and sparingly soluble salts obeys the mass action law if no other salts are present in the solution. Increasing the total amount of charged species in the solution causes a decrease in the distribution coefficients of calcium, the decrease being in accordance with a simple function of the concentrations of the sodium ion and the precipitating anion in solution. The relations between the adsorbability and the solubility products have also been derived.

THE possibility of dissolving sparingly soluble substances with the aid of Dowex A-1, the chelating ion-exchanger, has already been dealt with by Rich[1] in 1963. Rich showed that sparingly soluble salts of the alkaline earth metals, the heavy metals (Ag, Hg) and transition metals may be dissolved by this means within a relatively short time. In the present work this interaction was studied quantitatively and the connection between the solubility product of the salts and their adsorbability on the chelating ion-exchanger investigated. Such a system is difficult to evaluate because the equilibria have to be measured between two solid phases that are by no means easy to separate. On the other hand this system has distinct advantages in that over a certain range the composition of the solid species investigated is known and constant, as distinct from the equilibria in salt solutions in which there is invariably more than one species, a fact that complicates the equilibrium systems. The system resin–sparingly soluble salt–water has a favourable property from the point of view of kinetics, in that the concentration of metal ions is constant because it is controlled by the solubility product of the salt. In other words there is no concentration gradient, except perhaps in a very thin layer in the vicinity of the resin beads.

More recently[2] the influence of pH and ionic strength on the distribution coefficients of alkaline earths was investigated, and there the great reduction in metal ion adsorption at relatively low ionic strengths was stressed. In the present work the same effect was encountered, at yet smaller ionic strengths ($\mu = 0{\cdot}1$), and it was found that this reduction is proportional to $\sqrt{(Na^+)/(A^{2-})}$ (where A^{2-} = the precipitating anion). This mathematical relationship is not accidental; it is directly connected with the solubility products of calcium carbonate and oxalate.

EXPERIMENTAL

Reagents

Dowex A-1 chelating resin was purified by treatment with 2*M* hydrochloric acid and 2*M* sodium hydroxide, repeated three times. The end product, in its sodium form, was rinsed with demineralized water.

All other reagents were reagent-grade chemicals.

Equilibrium measurements

Portions (20 ml) of a solution containing 0·20 mmole of sodium hydroxide, 50 mg of calcium carbonate or oxalate, and varying quantities of the ligands (carbonate or oxalate) were added to 100-mg portions of the dried sodium form of the resin and placed in 100-ml Erlenmayer flasks. In a subsequent series of experiments the same batches were prepared but with the addition of varying quantities of sodium nitrate. All the solutions were shaken for a week at a temperature of 25°, after which the composition of the solution was found to remain unchanged. Resin and solution were then separated by passing them through a 200-mesh sieve which, however, also passed the small particles of the sparingly soluble salt present. Thorough rinsing in distilled water adequately separated the resin particles from those of the salts. The two phases were then examined as follows.

Resin phase. Calcium was extracted from the resin by four treatments with 5*N* hydrochloric acid at 70° and the excess of acid was removed by evaporation. Calcium was determined by titration with EDTA at pH 10, Erio-T being used as indicator in the presence of Mg-EDTA. Traces of heavy metals were apparently present in the resin, since it was necessary to add masking reagents, such as potassium cyanide and hydroxylamine, in order to obtain a sharp end-point.

The solutions from the EDTA titrations were evaporated to a small volume, organic matter was oxidized with sulphuric and nitric acids, and the mixed metal sulphates were obtained by evaporation and then weighed. Since the concentrations of magnesium, calcium, and the sodium from the EDTA were all known, the concentration of sodium was easily determined by subtraction.

The water content and swelling of the resin were determined. The bottoms of 7-ml polypropylene test-tubes were cut off and replaced by 200-mesh stainless steel sieves. These modified test-tubes were encased in normal glass test-tubes, filled with the resin and a quantity of the solution, and finally sealed in order to prevent evaporation. The liquid was centrifuged off and the resin washed with the solutions with which it had been in contact. A small portion of the resin beads was set aside for microscopic examination of size; the rest was dried and weighed.

Aqueous phase. The hydroxide and carbonate content were determined by potentiometric microtitration with hydrochloric acid and oxalate was determined by titration with potassium permanganate in acidic medium.

DISCUSSION AND RESULTS

Theoretical considerations

The reaction between Dowex A–1 and calcium carbonate or oxalate at high pH may be represented as a stoichiometric reaction of the type

$$2\overline{Na}^+ + \overline{R}^{2-} + \underline{CaA} \rightarrow \overline{CaR} + 2Na^+ + A^{2-} \qquad (1)$$

in which

R^{2-} = the resin anion (which includes iminodiacetic acid groups) of Dowex A–1 resin;
$A^{2-} = CO_3^{2-}$ or $C_2O_4^{2-}$.

The upper bars denote a species in the resin, and underlining signifies a precipitate.

If the experiment is repeated with constant quantities of resin and CaA, and varying quantities of the ligand A^{2-}, all being left for 7 days for equilibrium to be reached, the selectivity coefficient may be found. It may be also shown in this manner under which conditions a constant value, which is related to the composition of the system, can be obtained.

The thermodynamic equilibrium of reaction (1) is

$$E = \frac{(\overline{CaR})(Na^+)^2(A^{2-})}{(R^{2-})(\overline{Na}^+)^2} \qquad (2)$$

but because it is possible only to measure the mole fractions of the metals in the resin

and not the activities of the various components in it, a modified equilibrium coefficient must be defined:

$$E_{\text{mod}} = \frac{[\overline{\text{CaR}}](\text{Na}^+)^2(\text{A}^{2-})}{[\text{R}^{2-}][\overline{\text{Na}^+}]^2} = E\frac{f_{\text{R}^{2-}} f^2_{\text{Na}^+}}{f_{\text{CaR}}}.$$

From Table I it is clear that E_{mod} is not a constant, but increases to 2–3 times its initial value. This increase may be tentatively explained by the change occurring in the ratio $\frac{f_{\text{R}^{2-}} f^2_{\text{Na}^+}}{f_{\text{CaR}}}$ as the ligand concentration increases, and by changes in swelling.

Reaction (1) actually consists of three stages:

Dissolution: $$\text{CaA} \rightleftharpoons \text{Ca}^{2+} + \text{A}^{2-} \tag{3}$$

Chelation inside the resin: $$\overline{\text{Ca}^{2+}} + \overline{\text{R}^{2-}} \rightleftharpoons \overline{\text{CaR}} \tag{4}$$

Ion-exchange: $$2\overline{\text{Na}^+} + \text{Ca}^{2+} \rightleftharpoons 2\text{Na}^+ + \overline{\text{Ca}^{2+}}. \tag{5}$$

Reaction (3) may be controlled through the solubility product, although this is based on the assumption that no ion-pairs are formed—an assumption that has recently[3] been shown not to be always correct. Reaction (4) has without doubt an influence on $\frac{f_{\text{R}^{2-}} f^2_{\text{Na}^+}}{f_{\text{CaR}}}$ with the decrease of the adsorption of calcium by the resin. Reaction (5) is connected with the swelling and the contraction of the resin; its value may be estimated with the aid of Donnan's equation:[4]

$$E_{\text{Don}} = \frac{1}{Z_i F}\left(RT \ln \frac{(a_i)}{(\bar{a}_i)} - \Pi v_i\right) \tag{6}$$

in which

Z_i = charge on species i

F = the Faraday

a_i = activity of species i

Π = swelling pressure

v_i = partial molar volume of species i.

Substituting the activities of the two ions gives, in the present case:

$$\frac{(\text{Na}^+)^2\overline{(\text{Ca}^{2+})}}{(\overline{\text{Na}^+})^2(\text{Ca}^{2+})} = \exp\{\pi(2v_{\text{Na}^+} - v_{\text{Ca}^{2+}})/RT\} \tag{7}$$

and substituting (7) in the expression for E_{mod} produces

$$E_{\text{mod}} = \frac{f^2_{\text{Na}^+} f_{\text{R}^{2-}}}{f_{\text{CaR}}} \frac{K_{\text{CaA}}}{K_{\text{CaR}}} \exp\{\pi(2v_{\text{Na}^+} - v_{\text{Ca}^{2+}})/RT\}. \tag{8}$$

The partial molar volume of two sodium ions being larger than that of one calcium ion, the increasing sodium concentration inside the resin—as illustrated in Table I

TABLE I.—COMPOSITION AND EQUILIBRIUM DATA OF $CaCO_3$ AND CaC_2O_4 WITH DOWEX A-1

No.	Initial composition of the system			Resin composition at equilibrium			Solution composition at equilibrium			Calculated equilibrium		
	Resin in Na^+ form *g*	NaOH *mmole/ 20 ml*	Na_2CO_3 *mmole/ 20 ml*	$\bar{N}_{CaR}$ *mmole*	$\bar{N}_{R2-}$ *mmole*	$[Na^+]$ *mmole g.* of H_2O	$C_{CO_3^{2-}}$ *M*	pH	Ionic strength	$E_{mod} \times 10^{-5}$ *mole* l^{-1}	E_s *mole* l^{-1}	$E_{CO_3^{2-}}$ *mole* l^{-1}
1	0·100	0·20	0·00	0·185	0·048	0·90	0·0112	11·2	0·033	1·11	0·0393	0·0602
2	0·100	0·20	0·10	0·172	0·061	1·12	0·014	11·55	0·044	1·3	0·0378	0·0578
3	0·100	0·20	0·20	0·157	0·076	1·19	0·0179	11·72	0·058	1·68	0·0358	0·055
4	0·100	0·20	0·40	0·139	0·094	1·33	0·0271	11·67	0·083	2·94	0·0391	0·0557
5	0·100	0·20	0·60	0·110	0·123	1·50	0·0364	11·58	0·110	3·12	0·0315	0·0465
			$Na_2C_2O_4$ *mmole/20 ml*				$C_{C_2O_4^{2-}}$ *M*					$E_{C_2O_4^{2-}}$ *mole* l^{-1}
6	0·100	0·20	0·00	0·178	0·055	0·933	0·0089	11·15	0·029	0·795	0·0288	0·0442
7	0·100	0·20	0·10	0·168	0·065	1·10	0·0134	11·28	0·041	1·2	0·0346	0·0509
8	0·100	0·20	0·20	0·154	0·079	1·16	0·0177	11·27	0·055	1·6	0·0345	0·0476
9	0·100	0·20	0·40	0·127	0·106	1·42	0·0264	11·17	0·082	1·91	0·0317	0·0461
10	0·100	0·20	0·60	0·107	0·126	1·52	0·0354	10·81	0·106	1·9	0·0301	0·0428

(samples 1–5 and 6–10)—will cause a rise in the "osmotic" pressure difference, and E_{mod} will therefore also increase. A rough calculation shows that in these systems swelling effects change E_{mod} by only about 10%, so that it may be assumed to be influenced mainly by the changes in $\frac{f_{R^{2-}} f_{Na^+}^2}{f_{CaR}}$. The term f_{CaR} would be expected to be nearly constant, while the product of the activity coefficients of the "salt" Na_2R ($f_{R^{2-}} f_{Na^+}^2$) should principally express ion-association of sodium ions with the fixed groups of the resin. These interactions would become stronger with decreasing dielectric constant (*i.e.*, with increasing CaR concentration). From experiment 1 to experiment 5 CaR concentration decreases, so that $f_{Na^+}^2 f_{R^{2-}}$ should increase.

Another phenomenon which may be involved in this effect is the possibility of the formation of CaR_2. The first samples are strongly contracted, and each R^{2-} group is closely surrounded by CaR; CaR_2 may certainly form. Sides and Kenner[2] in some cases (alkaline earths) also found a molar ratio of 1:2.

Empirical constants

Consider the equilibrium between two "precipitates":

$$R^{2-} + \underline{CaA} \rightleftharpoons \overline{CaR} + A^{2-} \tag{9}$$

(In other words the standard state is defined as that in which the activity of sodium ions in the solution equals that in the resin.) $\underline{CaA}$ has a constant density; $\overline{CaR}$ is part of a solid solution; by using concentrations, the constancy of the selectivity coefficient E_s may be checked:

$$E_s = \frac{[\overline{CaR}][A^{2-}]}{[\overline{R}^{2-}]} = \frac{N_{CaR}[A^{2-}]}{N_{R^{2-}}} \tag{10}$$

Mole fractions (N_{CaR} and $N_{R^{2-}}$) can be used in this case instead of concentrations, because CaR and R^{2-} are always in the same volume of resin.

Again Table I shows a fairly good constancy of E_s with respect both to calcium carbonate (mean value 0·0367 mole l^{-1}) and to calcium oxalate (mean value 0·0319 mole l^{-1}), although the ionic strength in these systems varied from 0·033 to 0·11.

When the same experiments were attempted at a constant ionic strength of 0·11, obtained by adding the required amount of sodium nitrate, a sharp drop was seen to occur in the adsorption of calcium ions by the resin, while E_s was reduced to half the value shown in Table I. It was also seen that this drop was lessened with increasing A^{2-} concentration in the solution in equilibrium with the resin. Qualitatively these effects may be explained by the thermodynamic interdependence of E_s and E expressed by the formula

$$E_s = E \frac{f_{R^{2-}}(\overline{Na^+})^2}{f_{CaR} f_{A^{2-}}(Na^+)^2} \tag{11}$$

Increasing the activity of the sodium ions in the solution will not raise the activity of the sodium ion in the resin in the same proportion, since the concentration of sodium ions in the resin is large from the outset, so that any further increase is limited by electrolyte exclusion. An increase in sodium ion activity therefore reduces E_s. A

similar consideration applies to the activity of carbonate or oxalate in the solution, which controls the amount of calcium ions in the solution. The visible effect is that an increase in (A^{2-}), or decrease in (Ca^{2+}), raises E_s. The two effects cancel each other if the system contains only CaA with no excess of A^{2-}.

The results obtained from these experiments are best expressed as a function of $([Na^+]/[CO_3^{2-}])^n$, for which n was determined experimentally as $n = 1/2$. The results are summarized in Fig. 1.

The lines obtained in Fig. 1 are straight, with a slope of 1/2. Their intercept with the y-axis gives a new constant, E_A, which is characteristic of the anion concerned.

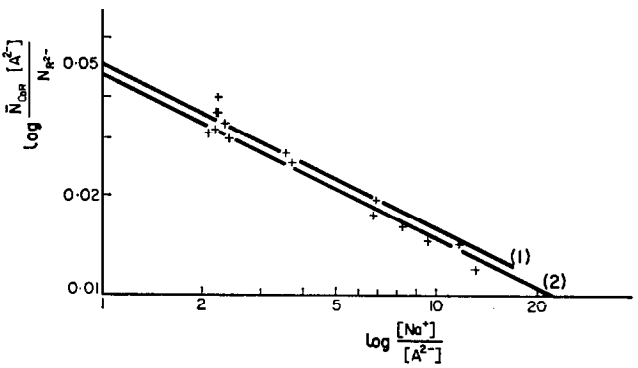

FIG. 1.—The influence of solution composition on the adsorbability of calcium on Dowex A-1.
(1) Calcium in the presence of carbonate ions.
(2) Calcium in the presence of oxalate ions.

$$E_A = E_s \left(\frac{[Na^+]}{[CO_3^{2-}]}\right)^{1/2} = \frac{N_{CaR}}{N_{R^{2-}}} \sqrt{[Na^+][CO_3^{2-}]}. \tag{12}$$

In practice the following values were obtained:

$$E_{CO_3^{2-}} = 0{\cdot}0518 \text{ mole } l^{-1}$$
$$E_{C_2O_4^{2-}} = 0{\cdot}0457 \text{ mole } l^{-1}$$

These values remain constant over a wide range of A^{2-} and sodium nitrate concentrations, as can be seen from Table I and was found in all the experiments done.

The connection between E_A and the solubility product

The connection between the mole fractions of the components in the resin and E_A was determined in equation (12). We may therefore write

$$\frac{E_{CO_3^{2-}}}{\sqrt{[Na^+][CO_3^{2-}]}} = \frac{N_{CaR}}{N_{R^{2-}}} = \frac{E_{C_2O_4^{2-}}}{\sqrt{[Na^+][C_2O_4^{2-}]}}. \tag{13}$$

In dilute solutions $f_{CO_3^{2-}} = f_{C_2O_4^{2-}}$ and therefore:

$$\frac{K_{spCaCO_3}}{K_{spCaC_2O_4}} = \left(\frac{E_{CO_3^{2-}}}{E_{C_2O_4^{2-}}}\right)^2. \tag{14}$$

The substitution of the numerical values obtained for $E_{CO_3^{2-}}$ and $E_{C_2O_4^{2-}}$ gives 1·28; Meites[6] gives 1·20 as the ratio between the solubility products—a reasonably good fit between a relatively involved experiment and a theoretical value.

CONCLUSIONS

Dowex A–1 is a chelating resin of low cross-linking in which the functional groups are fairly evenly distributed throughout the polymeric matrix. In view of this the resin may well be used in a way analogous to a chelating ligand in a solution, when the measure of similarity between two kinds of ligands is to be established.

In the present work it was shown that a connection exists between the stoichiometric reactions in the solution and the adsorbability on Dowex A–1. The connection between the overall concentration of electrolytes in the solution and the constants $E_{CO_3^{2-}}$ and $E_{C_2O_4^{2-}}$ is not haphazard, and many points over a wide range show the reliability of these values.

Experimental results from previous work,[5] carried out with soluble complexes with the purpose of examining the competition between copper glycinate and Dowex A–1 at pH 7 in the presence of varying quantities of potassium nitrate, may now be expressed by the reaction

$$H^+ + CuL_2 + R^{2-} \rightleftharpoons CuLR^- + HL \tag{15}$$

where HL is glycine.

The relationship found is

$$\frac{N_{CuLR}\sqrt{[K^+][HL]}}{N_{R^{2-}}[CuL_2]} = 116. \tag{16}$$

Here again the value remains constant over a wide range of concentrations.

Zusammenfassung—Die Wechselwirkung zwischen Dowex A–1 und schwer löslichen Salzen gehorcht dem Massenwirkungsgesetz, wenn keine anderen Salze in der Lösung vorhanden sind. Wächst die Gesamtmenge an geladenen Spezies in der Lösung, so fällt der Verteilungskoeffizient von Calcium; die Abnahme entspricht einer einfachen Funktion der Konzentrationen von Natrium und dem fällenden Anion in der Lösung. Auch die Beziehungen zwischen Adsorbierbarkeit und Löslichkeitsprodukten wurden abgeleitet.

Résumé—L'interaction entre la résine Dowex A–1 et des sels faiblement solubles obéit à la loi d'action de masse si d'autres sels ne sont pas présents dans la solution. Un accroissement de la quantité totale de l'espèce dont est chargée la solution cause une diminution des coefficients de partage du calcium, la diminution étant en accord avec une fonction simple des concentrations de l'ion sodium et de l'anion precipitant en solution. On a également calculé les relations entre l'adsorbabilité et les produits de solubilité.

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HIGH-SPEED COMPUTERS AS A SUPPLEMENT TO GRAPHICAL METHODS—V*

HALTAFALL, A GENERAL PROGRAM FOR CALCULATING THE COMPOSITION OF EQUILIBRIUM MIXTURES

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Summary—A computer program, HALTAFALL, is described which calculates the equilibrium concentrations of the species in mixtures of any number of components, which can form any number of complexes and solid phases, provided concentrations (or partial pressures) can be used in the equilibrium calculations. Of course, the equilibrium constants must be known and enough data be given about the gross composition. Some applications are indicated. The flexible input rules make it applicable to a variety of problems. From the input information, the program itself devises an efficient plan for solving the simultaneous equations. The program also provides an efficient means of finding out which of many possible solid phases can actually appear in a certain equilibrium mixture.

THE main task of "equilibrium analysis" is the study of *unknown* equilibria. One starts with a number of reagents, not knowing for sure what the main reactions between them are, and tries to design experiments and treat the results in such a way that one may deduce the main reactions, and their equilibrium constants. The earlier papers of this series,[1–4] and in the series on graphical methods,[5–8] have been devoted to problems with unknown equilibria.

However, even assuming that one *knows* what the main reactions and their equilibrium constants are, it is not always an easy task to calculate the concentrations of the various species in an equilibrium mixture with many interacting reactions. Traditionally, many chemists consider this type of calculation very difficult.

Graphical methods, especially logarithmic plots,[9,10] can give a good survey of even quite complicated systems, provided the equilibrium ratios between various species can be expressed as functions of one or two master variables, such as $\log\{H^+\}$, $\log\{e^-\}$, or $\log p(O_2)$. If a numerical computation is necessary, however, one would like to take advantage of the capacity of high-speed computers.

In part II of this series,[2] two computer programs, KUSKA and HALTA, were described for equilibrium calculations that could be reduced to solving equations for

* Part IV—*Arkiv Kemi*, 1964, **23**, 97; for comment on spelling "program" see *Talanta*, 1967, **14**, 833.

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one or two unknown master variables. Later on, we wrote similar programs for cases with a larger number of unknowns or other types of concentration conditions.

After some experience, however, we decided that we would rather have *one general program* for "known" equilibria than an increasing number of separate programs each for a special type of problem. A general program may not be quite as efficient as a program tailor-made for a special case, and hence may easily use more computer time. On the other hand, the general program saves the time otherwise needed for writing special programs, and computer time is getting less and less expensive in comparison with human time.

The first draft of this general ALGOL program—the new HALTA—was written by one of us (LGS) in late 1964, after discussions with NI on the types of equilibrium problems of interest to chemists. By the collaboration of NI and LGS improved editions were made to work on the computer BESK in Stockholm. WK took part in the work for three months in early 1965. When, in April 1965, NI and BW were to give a computer course for chemists at Göteborg University, they and LGS prepared an ALGOL version for SAAB D21. This program was then applied extensively to analytical problems by Professor David Dyrssen and his co-workers. Thanks to their work, some possible misbehaviours of the program were detected and corrected.

The first HALTA treated equilibria with only one fluid (liquid or gaseous) phase, but in 1965 it was extended to treat equilibria with one fluid and several solid phases. This revised program was called HALTAFALL, from the Swedish "halt" = concentration and "falla" = precipitate; a Scandinavian reader may find other associations as well. Starting with a draft by LGS the program was worked out on CD 3600 and CD 3200 by NI, BW and LGS. At the request of Dr Hay Liem, in December 1965 BW and LGS made additions so that HALTAFALL could also deal with distribution equilibria involving two fluid phases. Facilities for treating a gas phase at constant pressure were added as the need arose.

Many computer programs have been published for treating systems with "known" equilibria, and programs are still being published for surprisingly simple cases such as calculation of titration curves.

Most of the programs* of general interest that have been published are mainly designed and used for equilibria in a gas phase.[12–23] As will be discussed below, if condensed phases can be present, and the equilibrium conditions are known, one difficulty is to make the program deduce the correct set of condensed phases at equilibrium. This difficulty is avoided in most programs, either by considering only a gas phase, or by assuming that one has guessed the correct set; if the results are unreasonable, one may feed a new guess to the computer.[12–14] Villars's program[15] can decide whether or not solid carbon is present in a flame. Rosén[17] devised a more general method, and his special program decided which of three solid phases are present. Boll,[16] Cruise[21] and Shapiro[22] also handle cases with several condensed phases. The equilibrium conditions may either be set by minimizing the free energy (F or G) of the system,[11–13] or by applying equilibrium constant expressions.[14–23] A brief review of some important papers, including the iteration methods used, is given by Piehler.[18]

* Brinkley's procedure[14] was originally designed for computation by hand.

Programs for equilibria in a single liquid solution phase have been described by Anderegg,[24] Ropars and Viovy[25] and recently by Perrin.[26] The two first papers are in practice limited to three components, whereas the latter allows for an unlimited number of components. They all use equilibrium constants, and do not consider solid phases.

In comparison with other programs, it seems to us that HALTAFALL is very general and flexible, and is also adapted to the traditional ways of thought used by equilibrium chemists. It may be said to use the master variable approach (*cf.* ref. 9) like Ingri and Sillén[2] and Rosén,[17] and seems to converge reliably and quite rapidly even with very bad initial guesses for the master variables. We publish it here in the hope that it may be of some help to other chemists.

THE PROGRAM

Arrangement and Notation

Table I gives the present HALTAFALL program in ALGOL 60 with input/output orders mainly according to the ACM standard;[27] Table II explains the symbols used. Figures 3 and 4 are flow-sheets for essential parts of the program. The explanation of the principles in the text is mainly self-consistent but it may be advisable to glance occasionally at these tables and diagrams, even if explicit reference is not made to them.

The section on "input" is written in a manual style, and illustrated by the examples in Table III. For those who wish to test the program, the first output lines from the calculations are given.

The symbols in the text are partly defined as they appear and partly the same as in the ALGOL program (explained in Table II), where a quantity is often symbolized by a group of letters such as *Totbe*. The indices for a member of an array are sometimes given within square brackets, *pf*[*ia,if*] as in ALGOL, sometimes as a subscript, $pf_{ia,if}$. As usual, subscripts may mean things other than array numbers, but we trust there will be no misunderstanding. Matrices are denoted by bold-face letters; for a vector, an arrow may indicate whether it is horizontal or vertical.

Reference is sometimes made to Boolean (logical) variables (such as *Bra* below); as is well known, a Boolean variable has either of the values **true** or **false**.

One Fluid Phase

Species and equilibrium conditions

Let us start with a single fluid phase which may be a solution or a gas phase. Our system can be described with N_a *components* A_1, $A_2 \ldots A_{N_a}$, which can react to form N_X different products, *complexes*: $X_1, X_2 \ldots X_{NX}$.

In general it is convenient to choose as components well-defined species such as Ag^+, H^+, NH_3, $EDTA^{4-}$ in an aqueous solution, or $H_2(g)$, $CO(g)$, $O_2(g)$ in a gas phase. Sometimes it may prove practical to choose a component that does not correspond to a species present in measurable concentrations: e^-, H^+ in super-acidic solutions, C(s) or O(g) for a gas phase, *etc.* (for these, the Boolean *Noll*[*ia*] is set **true**).

We shall use the index *ia* to denote a component, and *ix* to denote a complex. By *p*[*ia*, *ix*] we mean the number of formula units of the component A_{ia} that are contained in the complex X_{ix}. Hence the composition of X_{ix} is

$$X_{ix} = (A_1)_{p[1,ix]}(A_2)_{p]2,ix]} \ldots . (A_{N_a})_{p[Na,ix]} \tag{1}$$

The numbers *p*[*ia*, *ix*] may be positive, zero, or negative; they are usually integers, but fractional numbers may appear. For instance, if Fe^{3+} and H^+ are among the components, a complex $Fe_2(OH)_2^{4+}$ in an aqueous solution is treated as $(Fe^{3+})_2(H^+)_{-2}$. If C(s) and $O_2(g)$ are components, CO(g) is $(C)_1(O_2)_{0.5}$. The activity of A_{ia}

$$\{A_{ia}\} = a_{ia} \tag{2}$$

is defined so that its ratio to the concentration $[A_{ia}]$ approaches indefinitely to unity when the composition of a solution approaches that of the solvent (or when the total pressure of a gas phase approaches zero). For components with *Noll*[*ia*], the ratio $\{A_{ia}\}/[A_{ia}]$ approaches instead an unknown constant $\gg 1$.

We shall assume that we can apply the law of ideality (activity = concentration) to all component species A_{ia} (if not *Noll*[*ia*]) and to all complexes X_{ix}. This assumption is usually permissible when

dealing with dilute gases, dilute solutions, or solutions in an ionic medium, and for approximate calculations. Provided one is consistent, the concentrations may be expressed in any convenient unit: mole fraction, mole/l, mole/kg or some pressure unit.

For the concentration of X_{ix}

$$c_{ix} = [X_{ix}], \tag{3}$$

the equilibrium law gives

$$\ln c_{ix} = \ln K_{ix} + p_{1,ix} \ln a_1 + \ldots p_{Na,ix} \ln a_{Na} = \ln K_{ix} + \sum_{ia} p_{ia,ix} \ln a_{ia} \tag{4}$$

where K_{ix} is the equilibrium constant for the formation of X_{ix} from the component species A_{ia}. Equation (4) uses natural logarithms as does the computer; for manual calculations, decadic logarithms are of course more convenient.

Mass balance equations

If the total concentration of each component is T_{ia} (in the program, *Tot*[*ia*]), the mass balance equations give

$$T_{ia} = a_{ia} + \sum_{ix} p_{ia,ix} c_{ix} \tag{5}$$

For components with *Noll*[*ia*], such as e^-, the activity a_{ia} may be well-defined, but does not correspond to the concentration of any component species, so that the term a_{ia} must be left out from (5). In either case, if the expressions for c_{ix} are inserted from (4), equation (5) gives each total concentration T_{ia} as a function of one, several, or all a_{ia}. The information on T_{ia} and a_{ia} may be given in various ways (input III). Often all one knows is the total concentration T_{ia} for each of the N_s components. One then has N_s equations (5), one for each component, from which the N_s unknown a_{ia} values can be deduced. For some purposes, *e.g.*, constructing survey graphs, it may be practical to consider a series of round values for some of the a_{ia} or log a_{ia} values. This reduces the number, N_{vs} of unknown a_{ia}, to be solved from equations (5) for each mixture considered.

Solving the equations (5)

So as not to overburden the reader with subscripts we shall change notation for a moment and denote the components by A, B, C . . . . their total concentrations by A, B, C . . . and the concentrations of the free component species by a, b, c . . . . Omitting the subscripts for p_i, q_i, *etc.*, we write any complex as

$$X_i = A_p B_q C_r \ldots \tag{1a}$$

Equations (4) and (5) take the forms

$$c_i = K_i a^p b^q c^r \ldots \tag{4a}$$

$$A = a + \sum p K_i a^p b^q c^r \ldots \tag{5a}$$

$$B = b + \sum q K_i a^p b^q c^r \ldots \tag{5b}$$

$$C = c + \sum r K_i a^p b^q c^r \ldots \tag{5c}$$

First let us consider how to solve the *equation for one component*, say (5*b*) for b, keeping a, c, *etc.* constant. On the right in equation (5*b*) is a monotonically rising function $B(b)$ since terms with positive or negative q all make B increase with increasing b. Here, then, is a special case of the general problem of finding the value for x that gives the value y_0 to a monotonically rising function $y(x)$. To solve it, HALTAFALL uses—in the switch ADA—the same operations as found after "Slinga" in Part IV of this series[4] (procedure Kålle in recent LETAGROP versions). For the same practical reasons as in Part IV, the $\ln a_{ia}$ are used as master variables rather than the a_{ia} themselves.

The computer starts with a first guess for $x(= \ln b)$, calculates $y(x)$ $[= B(b)]$ in procedure Totber and compares it with y_0 $(= B_{\text{given}})$. Then in successive passes through ADA series of systematic changes in x (symbolized here by Δx) and comparisons of the corresponding $y(x)$ with y_0 are performed. First, x is shifted by steps of 2 until one has one value for x that is too small and one that is too large. Then the computer interpolates, first by halving the interval of x, until it is smaller than a given value, "*stegbyt*", and finally by chords ("secant method") until the calculated y agrees with the given y_0 within the given tolerance limit *toly*. We have used this method extensively: it is reliable,

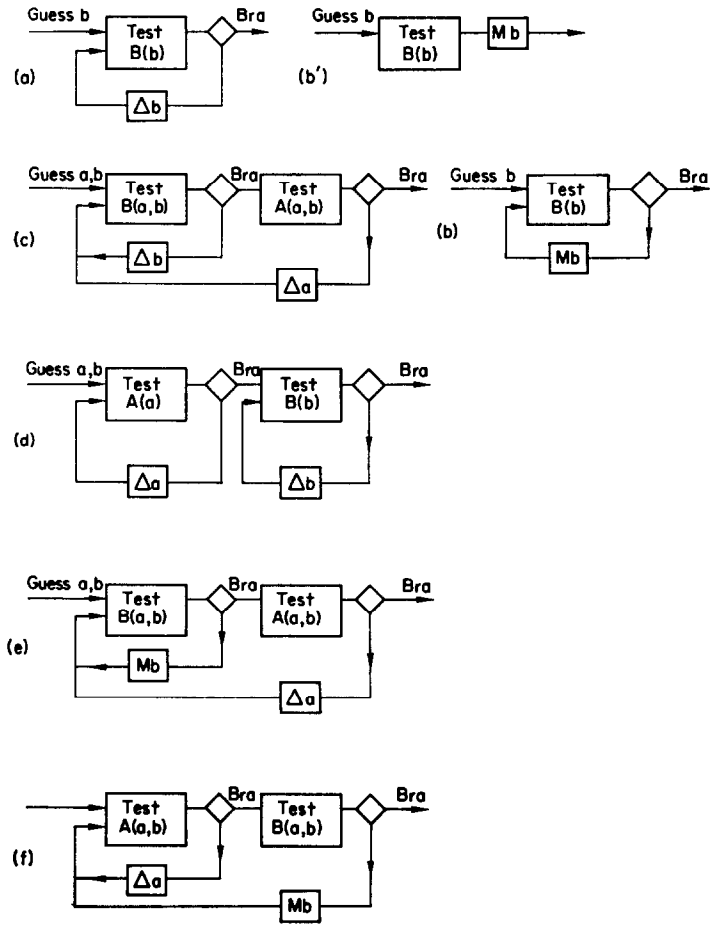

FIG. 1.—Some possible plans for solving equations (5) in equilibrium problems with one or two component concentrations (a, b) to be calculated from equilibrium conditions and total concentrations (A, B). See text for details; Δb stands for systematic variation by means of ADA, Mb for single step proportional adjustment in mononuclear cases.

general and quite fast, even with bad initial guesses, which we think makes it preferable to Newton-Raphson's method for the present case. We see no strong reason to change it, even if some economy of computer time might sometimes be achieved.

A special case occurs when B forms *only mononuclear* complexes (all q values are either 1 or 0) Then (5*b*) takes the form B = constant . b, and can be solved in one step, by a multiplication of the guessed value for b by the ratio $B_{\text{given}}/B_{\text{calculated}}$; this operation is symbolized here by Mb, or in general Mx.

Figure 1 symbolizes the method for the general case (Fig. 1*a*) and the mononuclear case (Fig. 1*b* and 1*b'*). We enter at the left with a guessed value for ln b. In the upper rectangle, $B(b)$ is calculated and tested for agreement of B_{calc} with B_{given}, within the tolerance limit. If there is agreement equation (5*b*) is satisfied, the Boolean *Bra* (Swedish = OK) is set *true*, and we proceed along the horizontal arrow to the right. Otherwise, in the general case ln b is changed (Δb), and $B(b)$ again calculated and tested (Fig. 1*a*). In the mononuclear case one might rely on the operation Mb to give immediately a correct result (Fig. 1*b'*). As it is, the program really makes one test (Fig. 1*b*) after making the operation Mb.

In a general case with *two unknowns*, a and b, and two functions, $A(a,b)$ and $B(a,b)$ to be adjusted to given values A_0 and B_0, Fig. 1*c* indicates a convenient method of solution. After ln b has been adjusted to make $B = B_0$, for a given ln$a$, a test is made for A, and ln$a$ is changed according to

whether A is found to be too small or too large. Then ln b is adjusted to make $B(a,b) = B_0$ with the new a value *etc.*, until both $A = A_0$ and $B = B_0$, within the given tolerance limits. At the end, ln a will have made a single cycle through ADA, whereas ln$b$ will have made many cycles. Permutation of A and B would give a schedule of the same type, and there is no *a priori* reason to prefer one or the other.

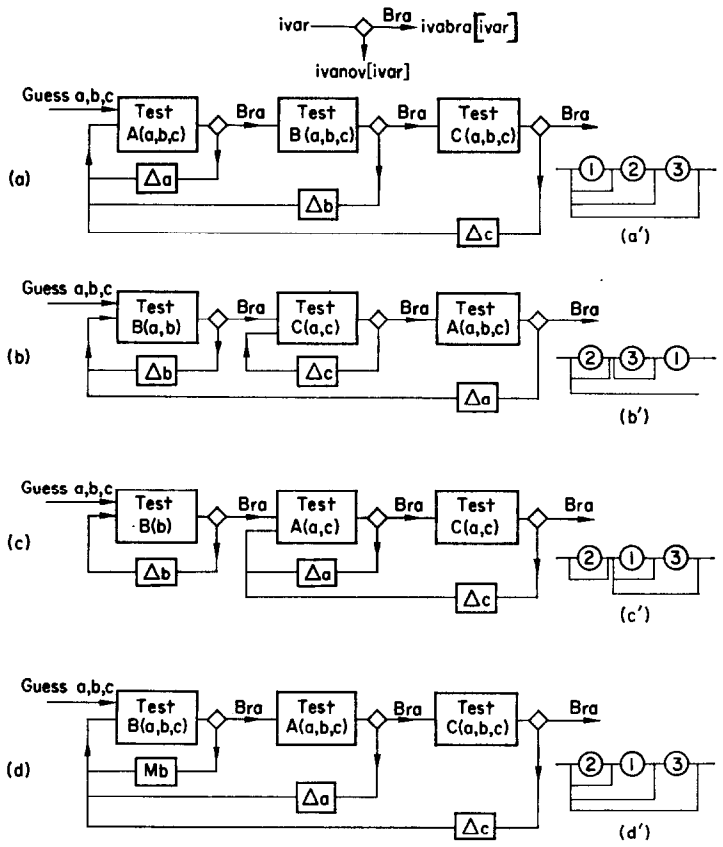

FIG. 2.—Possible plans for solving equilibrium problems with three component activities (a, b, c) to be determined from total concentrations A, B, and C and equilibrium conditions. M and Δ have the same significance as in Fig. 1. See text for details.

If the functions have the forms $A(a)$ and $B(b)$, then a and b are independent, and may be solved independently (Fig. 1*d*).

If B forms only mononuclear complexes, one might choose between the two schemes, Fig. 1*e* and Fig. 1*f*. The scheme in Fig. 1*e* requires only one ADA cycle for A and is hence preferred.

Figures 2*a*–2*d* similarly show convenient ways of solving the equations for cases with three components: a general case (Fig. 2*a*), no reaction B–C (no term containing both b and c, Fig. 2*b*), no reaction B–A or B–C (Fig. 2*c*), only mononuclear complexes with B (Fig. 2*d*). Permutation of A, B and C in Fig. 2*a*, of B and C in Fig. 2*b*, or of A and C in Fig. 2*c* or 2*d* would make no *a priori* difference.

If a mononuclear component is the first one to be tested, one may trust that the operation Mx will be successful. On the other hand, assume *e.g.*, that A in Fig. 2*b* is a mononuclear function. Then Δa will be replaced by Ma which like Δa affects B and C so that they have to be tested again. Hence the scheme in Fig. 2*b* will otherwise be the same, but it will work much faster if Ma can be used instead of Δa. A test is now made regularly after an M operation even if it happens to be the first.

In conclusion, one might attempt to set the general rules (1) that equations involving a smaller number of component activities should be tested before those with a larger number, and (2) that, everything else being equal, "mononuclear" equations should be tested before others.

Making the plan

Let us now return to the symbols A_1, A_2, A_3 etc for the components (A, B, C); T_1, T_2, T_3 for the total concentrations (A, B, C) and a_1, a_2, a_3 for the activities (free concentrations a, b, c), and remember that for practical reasons the computer treats the $\ln a_{ia}$ values as the unknowns in the equations. In the program, the symbol *ivar* is used for the *ia* number of the T_{ia} equation being tested, and hence of the $\ln a_{ia}$ that may as a result be varied; *e.g.*, if $ivar = 2$, T_2 is tested and $\ln a_2$ may be varied.

A plan like that in Fig. 1 or Fig. 2 may then be drawn in a still simpler form, giving the successive *ivar* numbers (Fig. 2*a'*–*d'*). The plan may be defined by two sets of numbers: (1) *iva*[1] to *iva*[*Nva*] are the *ivar* numbers in the order they should be tested; *Nva* is the number of unknowns. We set *iva*[*Nva* + 1] = 0, which serves as a signal that all equations (5) are satisfied; (2) *ivanov*[*ivar*] names the next *ivar* to be tested when the equation for T_{ivar} is not satisfied (*Bra* = **false**), so that $\ln a_{ivar}$ is adjusted by the operation Δ or M.

It is convenient to introduce also *ivabra*[*ivar*], the next *ivar* to be tested in case *Bra* = **true**. For instance, the plans in Fig. 2 (with *Nva* = 3) are described as follows. The numbers are *ia* numbers, *e.g.*, in Fig. 2*b*, *iva*[2] = 3, *ivabra*[2] = 3, and *ivanov*[2] = 2. Note that the index has a different meaning for *iva* on the one hand, and for *ivabra* and *ivanov* on the other. The statement *ivabra*[2] = 3 means that if the equation has been tested for *ivar* = 2 (thus the T_2 equation) and *Bra* found to be **true**, the next *ivar* to be tested is *ivar* = 3.

	iva[1 → 4]	*ivabra*[1 → 3]	*ivanov*[1 → 3]
Fig. 2*a*	1 2 3 0	2 3 0	1 1 1
Fig. 2*b*	2 3 1 0	0 3 1	2 2 3
Fig. 2*c*	2 1 3 0	3 1 0	1 2 1
Fig. 2*d*	2 1 3 0	3 1 0	2 2 2

(6)

Once the equations (5) are solved, the computer has the concentrations of all species and it is a trivial matter to ask it to print whatever quantities one wants to know: concentrations, logarithms of concentrations, average number of one component bound to another, *etc.*

The computer devises the plan of calculation from the information it has obtained on the *p*[*ia*,*ix*] for the various complexes. It uses two Boolean arrays, *Mono*[*ia*] which is **true** if A_{ia} takes part only in mononuclear complexes, and *Ober*[*i*,*j*] which is **true** if no complex contains both A_i and A_j, and hence a_i and a_j are "independent". For each component it calculates *Nober*[*ia*], the number of other components of which it is independent.

If there are N_{va} mass balance equations of type (5) to be solved, the computer arranges (after the label PLAN) the *ia* numbers of the corresponding components in the order, *iva*[1], *iva*[2] . . . *iva*[*Nva*], beginning with the *ia* that has the highest *Nober*, and for equal *Nober* beginning with those with *Mono*[*ia*] **true**; if *Nober* and *Mono* are equal, the lowest *ia* comes first. The *ivabra*[*ivar*] follow immediately from the *iva* series.

To find *ivanov*[*ivar*], the computer starts with *iva*[1], but if *iva*[1] is not connected with *ivar* (as seen from *Ober*), *ivanov* is shifted to *iva*[2], and so on.

After the plan has thus been laid out (and the necessary concentration data given) the computer can proceed to solve the equations for each "point", *i.e.*, equilibrium mixture. In Fig. 3, the full lines show the course of the calculation, from SLINGOR, the label where the first guesses for the $\ln a_{ia}$ are given, to the exit at FALLPROV, where all equations (5) are fulfilled. The broken lines refer to systems with solid phases present, which need not be considered until later.

To avoid unnecessary repetition, the calculation is made in three steps, using the procedures Lnbas, Cber and Totber. Lnbas calculates those parts of $\ln c_{ia}$ that are independent of $\ln a_{ivar}$, the $\ln a_{ia}$ to be varied. Cber calculates the concentrations c_{ia}. Totber combines the c_{ia} to give a calculated value y and compares it with the given $y_0 = Tot[ivar] = T_{ivar}$. If A_{ivar} is "mononuclear", Totber changes $\ln a_{ivar}$ by the operation we have denoted by M*x*.

Two Fluid Phases

If there are two fluid phases present—two liquids, or a gas and a liquid—the Boolean *Fas2* is set **true**. We can still use equilibrium conditions of the form (4) but if a certain chemical species occurs in both phases, we must treat it as a separate species in each phase. For each component A_{ia} we must hence decide in which phase to count it as a component species, with activity (concentration) a_{ia}; in the other phase, it is then treated as a complex with formation constant equal to its distribution constant.

Sometimes it may be practical to define the component species so that they are all in one phase, sometimes not. Suppose for instance that we are studying equilibria of a metal ion M^{s+}, a ligand acid HA (say dibutylphosphate—DBP), an uncharged ligand B (say tributylphosphate—TBP) and an

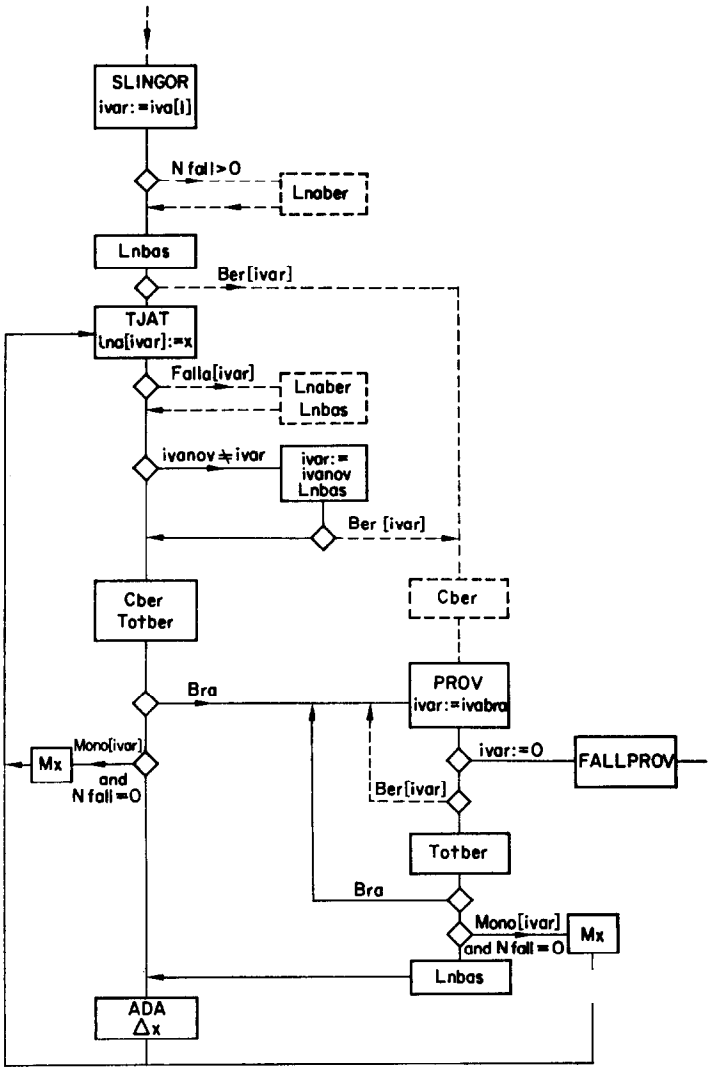

FIG. 3.—Flow sheet for solving the mass balance equations (5) or (16): enter at SLINGOR, exit at FALLPROV. The dotted lines are valid only in the presence of solid phases. Labels are written with capitals (SLINGOR, TJAT). The Boolean expression at a branching path such as *Nfall* > 0, *Bra*, or *Falla*[*ivar*] means that this path is taken if these Booleans are **true**. *Mx* stands for the "mononuclear" adjustment and Δx for the stepwise ADA adjustment, as in Figs. 1 and 2. The two branching points after **Totber** are inside the procedure Totber. In Lnbas one sets $x := lna[ivar]$.

inorganic anion X^- (say nitrate) in an aqueous phase and an organic phase. It may then be convenient to choose as component species: M^{s+}, H^+ and X^- in the aqueous phase, B in the organic phase, and HA in either the organic or the aqueous phase.

In the mass balance equations (5) we must consider the volumes of the two phases, V and V'. The total concentration T_{ia} may be defined as the amount of the component per unit volume of one phase (say the "unprimed" one) so that the total amount in the system is VT_{ia}. (Corresponding expressions are valid for concentration units other than mole/l.) On the other hand, the total amount of the component is obtained by multiplying each term to the right in equation (5) by V or V', depending on the phase in which the species occurs, and adding the products. If we finally divide this

expression by V, the resulting equation has the form (5) except that those concentration terms to the right that refer to the "primed" phase are multiplied by the volume ratio ϕ:

$$\phi = V'/V \tag{7}$$

The present program HALTAFALL is written for the case of equal volumes, $\phi = 1$. If ϕ is constant but differs from unity, one may simply, for all species in the primed phase, replace their K_{ix} by ϕK_{ix} and can then use (4) and (5) as before. By trivial changes in the program it could be adapted also to cases with varying volume ratio ϕ.

For calculating distribution ratios *etc.*, it is necessary to know in which phase each species occurs. For species in the "second" phase, the Boolean *Kifas2*[*ia*] (for A_{ia}) and *ifas2*[*ix*] (for X_{ix}) are **true**.

Gas Phase

Constant volume

For a single gas phase at constant volume, we may use the program in the same way as for a liquid solution provided we are careful with the concentration units. If the equilibrium constants are expressed in concentration units such as mole/l, then a_{ia}, c_{ix} and T_{ia} should be expressed in the same units. If one uses equilibrium constants with pressure units ("K_p"), then a_{ia}, c_{ix} and T_{ia} must be expressed in the same units, say bar, atm or possibly torr. Then a_{ia} and c_{ix} are the partial pressures, and T_{ia} is the pressure the component would have exerted if present alone, and in the form of the component species. (As is well known, to translate molar concentrations into pressures one multiplies by RT, being careful with the dimension of R.)

For the combination of a liquid phase and a gas phase at constant volume, again we may apply the program (setting *Fas2* **true**) but must be careful to make the dimensions of the K_{ix}, a_{ix} and c_{ix} consistent with the mass balance (5).

Constant pressure

For equilibria with a gas phase, it is often a practical condition that the total gas pressure be kept at a constant value, P_{tot}. In this case the Boolean *Pegas* is set **true**. The a_{ia}, c_{ix}, K_{ix} and T_{ia} are conveniently expressed in *pressure units*, as described for "constant volume".

The mass balance is usually defined by giving the mole ratios between the components (equivalent to the numbers of moles) *Ntot*[*ia*] $= n_{ia}$ in an initially unknown volume V of gas phase. The relationship is (note that T_{ia} is expressed in pressure units):

$$T_{ia} = n_{ia} * \left(\frac{RT}{V}\right) = n_{ia} * F. \tag{8}\dagger$$

F is an unknown, the same for all components. In the program, $\ln F$ is treated as another unknown, $\ln a[Na + 1]$, which is adjusted by means of an ADA cycle so as to satisfy, within the tolerance $\pm$ *tolp*, the total pressure condition

$$\sum a_{ia} + \sum c_{ix} = P_{\text{tot}}. \tag{9}$$

The test for (9) is made in the procedure Sump, after FALLPROV and NOG; if need be, F is changed, and the program returns to SLINGOR. This corresponds to another loop in Fig. 2, making in all $(N_{\text{va}} + 1)$ unknowns and is indicated in Fig. 4. The combination of a gas phase of constant pressure and variable volume, and a liquid phase, could be treated by trivial changes in the program, but no need has been seen for it as yet.

Ideal Liquid Mixture

For an ideal liquid mixture, one might use mole fraction units in a_{ia}, c_{ix}, T_{ia} and K_{ix}. We have an extra condition that the sum of all mole fractions = 1, which corresponds to (9) with $P_{\text{tot}} = 1$. Hence, the same treatment could be applied as for a gas at constant pressure.

Solid Phases Present

Up till now we have considered a single fluid phase, or possibly two, with variable concentrations of the species. Let us now assume that in addition a number N_f of solid phases are known, one or more of which might appear in our system at equilibrium. Each solid phase F_{if} is characterized by the coefficients *pf*[*ia*,*if*] of the components in its formula:

$$F_{if} = (A_1)_{pf[1,if]}\,(A_2)_{pf[2,if]} \ldots (A_{Na})_{pf[Na,if]}. \tag{10}$$

† The symbol * written on the line is ALGOL for *multiply*.

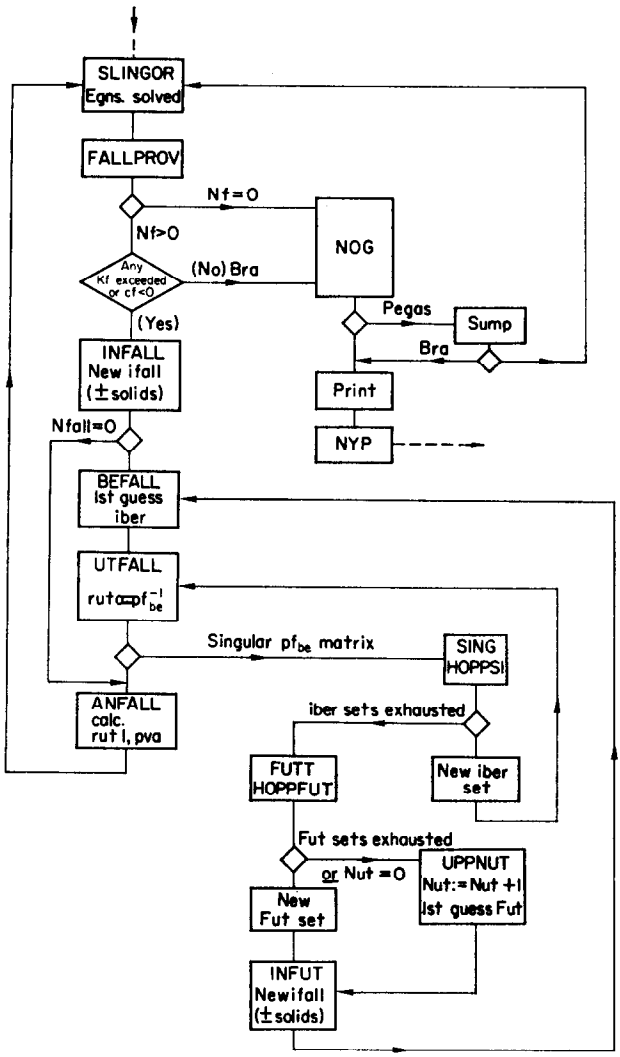

FIG. 4.—Plan for finding out which solids are present at equilibrium.

The coefficients *pf* may be positive or negative, integers or fractions. If Kf_{if} is the equilibrium constant (solubility product) for the dissolution of solid F_{if} to form the components, then the condition for F_{if} to be at equilibrium with the solution is

$$\ln Kf_{if} = pf_{1,if} \ln a_1 + \ldots + pf_{Na,if} \ln a_{Na} = \sum_{ia} pf_{ia,if} \ln a_{ia}. \tag{11}$$

These equations may give some new interdependences between components, which must be considered when calculating *Ober*[*i*, *j*].

The mass balance equations (5) are replaced by a set of equations (12), containing the formal concentrations cf_{if}, meaning the number of moles of solid F_{if} present per litre of solution (or correspondingly for other concentration units):

$$T_{ia} = a_{ia} + \sum_{ix} p_{ia,ix} c_{ix} + \sum_{if} pf_{ia,if} cf_{if}. \tag{12}$$

For the c_{ix}, (4) is valid as before.

Suppose that we know which solid phases are present, altogether N_{fall} phases, with the *if* numbers

ifall[1] to *ifall*[*Nfall*]. To find the a_{ia}, we have N_{fall} equations (11), one for each solid, and N_a equations (12), one for each component. The values of the N_{fall} formal concentrations cf_{if} are usually not interesting (as long as they are positive), and they may be eliminated from (12), leaving N_{fall} equations (11) and N_{vaf} reduced equations (16) (see below) of the same type as (5) where

$$(N_{vaf} = N_{va} - N_{fall}). \tag{13}$$

In other words, only N_{vaf} of the a_{ia} need to be calculated by solving equations of type (5) whereas the others can be found by applying (11). We may then divide the a_{ia} into three classes.

I. As before, $(N_a - N_{va})$ of the a_{ia} values are known from the onset.

II. N_{vaf} of the a_{ia} values are to be calculated from reduced mass balance equations of type (5); their *ia* numbers will be denoted by *ivaf*[1] to *ivaf*[*Nvaf*], in the order in which they will be solved.

III. N_{fall} of the a_{ia} values will be calculated from equilibrium conditions of type (11). Their *a*] numbers will be denoted by *ibe*[1] to *ibe*[*Nfall*], and for these *ia* (but no others) the Boolean *Ber*[*iia* is **true**.

The equations we need are perhaps best deduced in matrix form. The N_{fall} equations (11) and the N_a equations (12) may be written

$$\vec{\mathbf{ln\ Kf}} = \vec{\mathbf{ln\ a}} * \mathbf{pf} \tag{11m}$$

$$\underset{\downarrow}{\mathbf{T}} = \underset{\downarrow}{\mathbf{a}} + \mathbf{p} * \underset{\downarrow}{\mathbf{c}} + \mathbf{pf} * \underset{\downarrow}{\mathbf{cf}} \tag{12m}$$

The dimensions (rows, columns) of the matrices above are: $\mathbf{ln\ Kf}(1, N_{fall})$, $\mathbf{ln\ a}(1, N_a)$, $\mathbf{pf}(N_a\ N_{fall})$, $\mathbf{T}$ and $\mathbf{a}(N_a, 1)$, $\mathbf{p}(N_a, N_x)$, $\mathbf{c}(N_x, 1)$, $\mathbf{cf}(N_{fall}, 1)$.

We may divide (11*m*) into two parts, "be" corresponding to the ln a_{ia} of class III above, and "not-be" corresponding to classes I + II.

$$\vec{\mathbf{ln\ Kf}} = \vec{\mathbf{ln\ a}}_{\mathbf{be}} * \mathbf{pf}_{\mathbf{be}} + \vec{\mathbf{ln\ a}}_{\mathbf{not\text{-}be}} * \mathbf{pf}_{\mathbf{not\text{-}be}} \tag{11m'}$$

In the dimensions of the matrices, N_a is replaced by N_{fall} for "be" and by $(N_a - N_{fall})$ for "not-be". It follows from (11*m*') that we may calculate $\mathbf{ln\ a_{be}}$ from

$$\vec{\mathbf{ln\ a}}_{\mathbf{be}} = \vec{\mathbf{ln\ Kf'}} * \mathbf{pf}^{-1}{}_{\mathbf{be}} \tag{14}$$

where $\mathbf{lnKf'}$ is a reduced vector (*ln Kmi* in Lnaber).

$$\vec{\mathbf{ln\ Kf'}} = \vec{\mathbf{ln\ Kf}} - \vec{\mathbf{ln\ a}}_{\mathbf{not\text{-}be}} * \mathbf{pf}_{\mathbf{not\text{-}be}} \tag{14a}$$

Equations (14*a*) and (14) are used in the first part of the procedure Lnaber, and $\mathbf{pf}_{be}^{-1} = ruta$ is calculated after UTFALL.

The mass balance equations (12*m*) may be written separately for the N_{fall} "be" components (class III) and for the N_{vaf} "vaf" components (class II)

$$\mathbf{T}_{be} = \mathbf{a}_{be} + \mathbf{p}_{be} * \mathbf{c} + \mathbf{pf}_{be} * \mathbf{cf} \tag{12a}$$

$$\mathbf{T}_{vaf} = \mathbf{a}_{vaf} + \mathbf{p}_{vaf} * \mathbf{c} + \mathbf{pf}_{vaf} * \mathbf{cf}. \tag{12b}$$

Eliminating **cf** from (12*a*) we find

$$\mathbf{cf} = \mathbf{pf}_{be}^{-1} * (\mathbf{T}_{be} - \mathbf{a}_{be} - \mathbf{p}_{be} * \mathbf{c}) \tag{15}$$

Introducing (15) into (12*b*) we get a matrix equation, equivalent to N_{vaf} equations of the same type as (5).

$$\underset{\downarrow}{\mathbf{T'}_{vaf}} = \underset{\downarrow}{\mathbf{a}_{vaf}} + \underset{\downarrow}{\mathbf{p'}_{vaf}} * \mathbf{c} \tag{16}$$

where the reduced $\mathbf{T}$ and $\mathbf{p}$ may be calculated from

$$\mathbf{T'}_{vaf} = \mathbf{T}_{vaf} - \mathbf{pf}_{vaf} * \mathbf{pf}_{be}^{-1} * (\mathbf{T}_{be} - \mathbf{a}_{be}) \tag{16a}$$

$$\mathbf{p'}_{vaf} = \mathbf{p}_{vaf} - \mathbf{pf}_{vaf} * \mathbf{pf}_{be}^{-1} * \mathbf{p}_{be}. \tag{16b}$$

The N_{vaf} reduced mass balance equations (16) and the N_{fall} reduced equilibrium equations (14) should suffice for calculating the N_{va} unknown a_{ia}.

The "be" components can often be selected in several ways. Obviously, one cannot allow a selection that would give a zero determinant to $\mathbf{pf}_{be}$ since then it could not be inverted as required by (14), (16*a*) and (16*b*).

At present the program is based on the plan (= the set of *iva, ivanov* and *ivabra*) devised for the absence of solid phases. At first it is assumed (at BEFALL) that the first N_{fall} of the *iva* are the *ibe* to be calculated. If the determinant of $\mathbf{pf}_{be}$ is found to be zero at UTFALL, the *ibe*'s are changed systematically (at SING-HOPPSI), by means of the array *iber*, until a non-zero determinant is found. Then, at ANFALL, $\mathbf{pf}_{vaf} * \mathbf{pf}_{be}^{-1}$ (= *rut*1) and $\mathbf{p}'_{vaf}$[= "*pva*", equation (16*b*)] are calculated.

The course of the following calculations is shown by the diagram, Fig. 3, this time including the broken lines. Whenever a $\ln a_{ia}$ from the "vaf" class has been changed, all those of the "be" class are recalculated, using Lnaber [equation (14)], which also recalculates the T'_{vaf} ("*Totva*") since they contain a_{be} [equation (16*a*)]. The right hand side of (16) is compared with T'_{vaf} in Totber. On the other hand, if a new *ivar* belongs to the "be" class, one just passes to *ivabra*[*ivar*].

Possibly the most rapid procedure for some case may differ from the one now taken; at any rate, the equations are in general solved much faster in the presence of solid phases than without them.

Test for consistency

After a set of $\ln a_{ia}$ have been found that satisfy equations (14) and (16), one must test that they are consistent with the assumptions made as to which phases are present. Hence, (1) the solubility product *Kf* (11) must not be exceeded for any phase assumed to be absent, (2) the "formal concentration" *cf*, calculated by (15), must not be negative for any solid phase assumed to be present. These two tests are made after the label FALLPROV. (See the plan in Fig. 4.)

If the set of $\ln a_{ia}$ proves consistent, *Bra* comes out **true**, and the computer proceeds to NOG (= enough), otherwise it passes the labels INFALL, BEFALL and UTFALL, where it adds or subtracts solids as indicated by FALLPROV, and tries various sets of *iber*. When it has found a $\mathbf{pf}_{be}$ that can be inverted it goes to ANFALL, calculates the matrices *ruta* = $\mathbf{pf}_{be}^{-1}$, *rut*1 = $\mathbf{pf}_{vaf} * \mathbf{pf}_{be}^{-1}$ and *pva* = $\mathbf{p}'_{vaf}$ (16*b*), after which it goes back to SLINGOR.

At NYKO where K_{ix} and K_{if} are given it is assumed that no solid is formed. For the first point the equations (5) are solved (SLINGOR) and the set of $\ln a_{ia}$ tested for consistency. If necessary, solid phases are added and subtracted until a consistent set is obtained. For the next point in the series one starts by assuming that the same solid phases are present as at the preceding point, *etc.*

For instance, if we start with a solution containing Cl^-, Br^- and I^-, and add a small amount of Ag^+, the first hypothesis "no solid phase" gives ln a_{ia} values which exceed the solubility products of AgCl, AgBr and AgI. The second hypothesis, that these three solids are present, gives a negative formal concentration *cf* of AgCl. This is easily understood: at equilibrium with these three phases, $[Cl^-]:[Br^-]:[I^-] \approx 360:1:0{\cdot}0002$ so that most Br^- and I^- must be precipitated as AgBr and AgI. This would require the addition of a large amount of AgCl(s) from the outside, hence a negative *cf* for AgCl.

In the next cycle, AgCl is hence struck out. The third hypothesis, AgBr and AgI present, gives a negative *cf* for AgBr, and we are left with only AgI(s), which gives a consistent set of ln a_{ia}. If enough Ag^+ is added, however, AgBr(s) and AgCl(s) will also appear at equilibrium.

Provision has also been made for the more complicated case where FALLPROV indicates a set of solid phases which are not compatible at all. This may occur if there are two solid phases of the same composition, with different solubility products, or more generally if there is a linear relationship between the composition of a group of solid phases, or if more solids are indicated than there are ln a_{ia} values to vary. In such cases it proves impossible to pick out a group of N_{fall} components "*ibe*" such that $\mathbf{pf}_{be}$ has a non-zero determinant. When this has been found, one must try systematically combinations of a smaller number ($N_{fall} - N_{ut}$) of solid phases, until a consistent solution is found. This is done at FUTT, INFUT and UPPNUT, using the array *Fut*. To avoid going into a loop, the computer sets the Boolean *Singfall* **true** and remembers the first set of solids (*ifspar*[1] to *ifspar*[*Nfspar*]) which gave only zero determinants; it then automatically returns to "striking out" solids systematically until a consistent solution of the problem is found.

INPUT

O. Optional

(0:1) Orders for printing text, *e.g.*, characterizing the problem: 0, 0, followed by card with text. This may be repeated: 0,0,/text/0,0,/text/*etc.* For tape input, this can be done in other ways, depending on the computer.

(0:2) Ending the calculation: −1, −1,

I. Equilibrium data

(I:1) Number of components: *Na*, (if there are two fluid phases, give instead *Na* + 1).

(I:2) Data on soluble complexes: Nx, (*kbas, pot*, $(p[ia, ix])_{Na})_{Nx}$,†

† The subscript outside a parenthesis states how many such quantities or sets of quantities must be given.

The equilibrium constants are given by $K_{ix} = kbas*10^{pot}$. If there are two fluid phases, give $-Nx$ instead of Nx, and for each species add $p[Na + 1, ix]$, which is 1 if the species is in the second phase, otherwise 0.

(I:2a) If there are two fluid phases, add, immediately after Nx: m, $(ia)_m$, where m is the number of components with activities set equal to their concentrations in the second phase, and after m their ia numbers are given.

(I:3) Data on solid phases: Nf, $(kbas, pot, (pf[ia, ix])_{Na})_{Nf}$.

Again, the solubility product is given as $Kf = kbas*10^{pot}$. If no solid phase:0.

II. Printing orders

$Npri$, $(prix_1, prix_2)_{Npri}$,

Each of the N_{pri} printing orders consists of two integers, $prix_1$ and $prix_2$, which have the following significance:

$prix_1$	$prix_2$	quantity to be printed
ix	1	c_{ix}
ix	2	log c_{ix}
ix	$-ia$	$p_{ia,ix}*c_{ix}/T_{ia}$, fraction of A_{ia} present in complex X_{ix}
0	0	V_T, volume added in titration
$-ia$	1	a_{ia}
$-ia$	2	log a_{ia}
$-ia$	3	log (T_{ia}/a_{ia})
$-ia$	4	T_{ia}
$-ia$	5	a_{ia}/T_{ia}
$-ia$	6	log D_{ia}, log of distribution ratio for component A_{ia}
$-ia$	7	$D_{ia}/(1 + D_{ia})$
$-ia$	$-m$	average number of A_{ia} bound per A_m

III. Concentration data

These data are given as follows: III:1, (III:2, (III:3)$_{Np}$)$_{Ns}$.

The task to be carried out is divided into Ns groups. Each group contains a certain number Np of points, each of which corresponds to an equilibrium mixture. The type of concentration data may be different in different groups, but throughout the Ns groups the same equilibrium data and the same printing orders are valid.

(III:1) Common data: Ns, *stegbyt*.

Stegbyt is the value for *steg* in ADA at which "chord shooting" should replace binary approach. It may conveniently be set equal to the reciprocal value of the highest $p[ia, ix]$ value represented.

(III:2) Group data: Np, (*hur*[*ia*] + 0–4 numbers, see list below)$_{Na}$, (*Ptot*, *tolp*)(if *Pegas*), V_0 (if *Titer*).

Instead of Np, the number of points, $-Np$ is given if we treat a gas mixture at constant pressure. *Pegas* is then set **true**.

The series of numbers, *hur*[1] to *hur*[*Na*] tells what type of concentration data will be given for the corresponding component A_{ia}. After each *hur*[*ia*] come 0–4 numbers, as follows, with notations as in the program:

1, *start*[*ia*], *tol*[*ia*], *Tot*[*ia*]; for *hur* = 1, T_{ia} = *Tot*[*ia*] is constant throughout the group, and is to be printed.

2, *start*[*ia*], *tol*[*ia*], *Tot*[*ia*], *step*[*ia*]; for *hur* = 2, *Tot*[*ia*] starts at the given value and is then varied by steps, *step*[*ia*].

3, *start*[*ia*], *tol*[*ia*]; then *Tot*[*ia*] will be given for each point separately.

4, *start*[*ia*], *tol*[*ia*], A_0[*ia*], *AT*[*ia*]; titration—to V_0 ml of solution with $T_{ia} = A_0$[*ia*] one adds V_T ml of a solution with $T_{ia} = A_T$[*ia*] so that *Tot*[*ia*] = $(A_0*V_0 + A_T*V_T)/(V_0 + V_T)$.

5, log a_{ia}; then log a_{ia} is constant throughout group, to be printed.

6, log a_{ia}, step log$_{ia}$; then log a_{ia} starts as log a_{ia} and is then varied by steps, steplog $_{ia}$.

7, then log a_{ia} will be given at each point.

For *hur*[*ia*] < 5 only the total concentration *Tot*[*ia*] is known so that a_{ia} must be calculated from equation (5). One must then also give *start*[*ia*], which is the first guess for ln a_{ia}, and *tol*[*ia*] which indicates the deviation in T_{ia} (calculated), "*toly*", that we may tolerate when solving equation (5). If *tol*[*ia*] is given as a positive number, *toly*[*ia*]: =*tol*[*ia*]; if *tol*[*ia*] < 0, *toly*[*ia*]: =abs(*tol*[*ia*]*Tot*[*ia*]). If T_{ia} may be zero or negative, a positive *tol*[*ia*] must be used since one may otherwise soon get stuck in a loop.

Hur[*ia*] is set negative (for instance, −6, *loga*[*ia*], *steplog*[*ia*]) if *Noll*[*ia*] is **true**, hence the term a_{ia} is to be excluded from the expression (5) for the total concentration T_{ia}.

If *Pegas* is **true** (gas at constant pressure), one gives P_{tot} and the tolerance *tolp* for solving (9).

If at least some *hur*[*ia*] = 4, then a titration is considered, *Titer* is **true** and V_0 is given.

(III:3). Point data: V_T (if *Titer*), *Tot*[*ia*] (if *hur* = 3), *loga*[*ia*] (if *hur* = 7). If *hur* was 3 or 7 for some components, the promised values for *Tot*[*ia*] or *loga*[*ia*] are given, in the order of increasing *ia*. If not, and if in addition *Titer* is **false**, no point data are needed.

After I + II + III have been given, one may either start a new equilibrium problem with 0:1 and I, or finish the calculation by 0:2.

EXTENDING OR REDUCING THE PROGRAM

By changing the dimensions of the arrays, one may allow a practically unlimited number of reagents and complexes, although the amount of calculation may increase very much with increasing N_a and N_x.

The program—as far as we know—can handle the equilibria in systems that follow the ideal laws for dilute gases or solutions, that involve any number of solids and in addition one or two fluid phases at constant volume, a gas phase at constant pressure, or an ideal fluid mixture.

To adapt the program to other combinations, *e.g.*, more than two fluids with varying volume, solid solutions, *etc.*, one would have to make changes in the input and the calculation of the T_{ia}, but no new principal difficulties are expected. Likewise, by trivial changes one may ask for additional quantities to be printed, such as the *cf.*

Bringing variable activity factors into the picture would, of course, necessitate new loops.

The present program may also be abbreviated. Those who know that they will never want to study problems with solid phases, or with two fluid phases, or to have certain types of quantities printed, may remove the corresponding parts of the program. The exclusion of solid phases especially will make it considerably shorter.

TABLE I.—HALTAFALL (MARCH 1967)

```
begin comment Haltafall;
real det, F, kbas, lnc, ln10, Ptot, stegbyt, tolp, V0, VT, Vtot, x, y, y0, w, wl;
integer i, ia, if, ivar, ix, j, m, Na, Nf, Nfall, Nfspar, Np, Npri, Ns, Nut, Nva, Nvaf, Nx, Nyfall, pot,
    Rp, Rs, Rva;
Boolean Bra, Fas2, Pegas, Singfall, Titer;
real array A0, AT, lna, Ntot, start, steg, step, tol, toly, Tot, Totbe, Totmi, Totva, x1, x2, y1, y2[1:8],
    lnKf, lnKmi[1:10], pf[1:8, 1:10], p, pva[1:8, 1:20], ruta, rut1[1:5, 1:5], skriv[1:20], c, lnba
    lnbeta[1:20];
integer array fut, Hur, ibe, iber, ifall, ifspar, iva, ivabra, ivaf, ivanov, Karl, Nober[1:8], prix[1:20,
    1:2], tryn[1:20];
Boolean array Fall[1:10], Ber, Falla, Kifas2, Mono, Noll[1:8], ifas2[1:20], Ober[1:8, 1:8];
switch ADA:=Ada1, Ada2, Ada3, Ada4, Ada5, Ada6, Ada7;
switch HURSA:=Hur1, Hur2, Hur3, Hur4, Hur5, Hur6, Hur7;
switch PBER:=Pber1, Pber2, Pber3, Pber4, Pber5, Pber6, Pber7;
switch TRYCKA:=Tryck1, Tryck2, Tryck3, Tryck4, Tryck5, Tryck6, Tryck7, Tryck8, Tryck9
    Tryck10, Tryck11, Tryck12;

procedure Cber; begin
    for ix:=1 step 1 until Nx do begin lnc:=lnba[ix] + p[ivar, ix]*lna[ivar];
    if lnc > 10 then c[ix]:=20000;
    else if lnc < −23 then c[ix]:=0 else c[ix]:=exp(lnc) end end Cber;

procedure Invert (N, A, eps, det, Sing); = in part IV.[4]
```

```
procedure Lnaber; begin
    for i:=1 step 1 until Nfall do begin
      if:=ifall[i]; w:=lnKf[if];
      for ia:=1 step 1 until Na do not if Ber[ia] then w:=w − pf[ia, if]*lna[ia];
      lnKmi[i]:=w end;
    for i:=1 step 1 until Nfall do begin w:=0; ia:=ibe[i];
      for j:=1 step 1 until Nfall do w:=w+lnKmi[j]*ruta[j,i];
      lna[ia]:=w; Totmi[i]:=if Noll[ia] then Tot[ia] else Tot[ia]-exp(w) end;
    for i:=1 step 1 until Nvaf do begin ia:=ivaf[i]; w:=Tot[ia];
      for j:=1 step 1 until Nfall do w:=w−rut1[i,j]*Totmi[j];
      Totva[ia]:=w end end Lnaber;
procedure Lnbas; begin
    x:=lna[ivar];
    for ix:=1 step 1 until Nx do begin lnba[ix]:=lnbeta[ix];
      for i:=1 step 1 until Na do
      if i≠ivar then lnba[ix]:=lnba[ix]+p[i,ix]*lna[i] end end Lnbas;

procedure Sump; begin
    y:=0;
    for ia:=1 step 1 until Na do
      if not Noll[ia] then y:=y+exp(lna[ia]);
      for ix:=1 step 1 until Nx do y:=y+c[ix];
      if abs(y−Ptot) > tolp then begin
        y0:=Ptot; ivar:=Na+1; x:=lna[ivar];
        goto ADA[Karl[ivar]] end
    end Sump;

procedure Totber; begin
    if Noll[ivar] then y:=0 else y:=exp(lna[ivar]);
    if Nfall = 0 then begin for ix:=1 step 1 until Nx do y:=y+p[ivar,ix]*c[ix] end
      else for ix:=1 step 1 until Nx do y:=y+pva[ivar,ix]*c[ix];
      comment y =Totber[ivar];
    if Nfall = 0 then y0:=Tot[ivar]
      else begin y:=y−Totva[ivar]; y0:=0 end;
    w:=abs(y−y0);
    if toly[ivar] > w then begin comment Bra; Karl[ivar]:=1; goto PROV end
      else
    if Mono[ivar] and Nfall =0 then begin x:=lna[ivar]:=
      lna[ivar]+ln(y0)−ln(y); goto TJAT end end Totber;

      output (61,'/,'HALTAFALL");
      ln10:=ln(10);

NYKO:       input (60,'2(N)',Na,Nx);
            if Na < 0 then goto SLUT;
            if Na = 0 then begin
                output (61,'/'); input (60,'/');
              for i:=1 step 1 until 80 do begin
                input (60,'A',m); output (61,'A',m);
                end
              goto NYKO end;
            Nfall:=0;
            for ia:=1 step 1 until Na do Ber[ia]:=Falla[ia]:=false;
            if Nx < 0 then begin Fas2:=true; Nx:=−Nx;
              for ia:=1 step 1 until Na do Kifas2[ia]:=false;
                input (60,'N',m);
              for i:=1 step 1 until m do begin
                input (60,'N',ia);
              Kifas2[ia]:=true end
              end
            else Fas2:=false;
                output (61,'/,4ZD,B,'LÖSTA",Nx);
```

```
          for ix:=1 step 1 until Nx do begin
              input (60,'2(N)',kbas,pot);
            if kbas > 0 then lnbeta[ix]:=ln(kbas)+pot*ln10
            else lnbeta[ix]:=-1000;
            for ia:=1 step 1 until Na do
              input (60,'N',p[ia,ix]);
            if Fas2 and p[Na,ix] = 1 then ifas2[ix]:=true
            else ifas2[ix]:=false;
              output (61,'/,3ZD.3D,-4ZD',kbas,pot);
            for ia:=1 step 1 until Na do
              output (61,'-2ZD.2D',p[ia,ix])
          end;
          if Fas2 then Na:=Na-1;
          for ia:=1 step 1 until Na do begin Mono[ia]:=true;
            for ix:=1 step 1 until Nx do begin m:=p[ia,ix];
              if m ≠ 0 or m ≠ 1 then Mono[ia]:=false end end;
              input (60,'N',Nf); output (61 '/,4ZD,B'FASTA",Nf);
          for if:=1 step 1 until Nf do begin Fall[if]:=false;
              input (60,'2(N)',kbas,pot);
              output (61,'/,3ZD.3D,-4ZD',kbas,pot);
            lnKf[if]:=ln(Kbas)+pot*ln10;
            for ia:=1 step 1 until Na do
              input (60,'N',pf[ia,if]);
            for ia:=1 step 1 until Na do
              output (61,'-ZD.2D',pf[ia,if]);
          end;
          for i:=1 step 1 until Na do for j:=1 step 1 until Na do begin
            Ober[i,j]:= if i = j then false else true;
            for ix:=1 step 1 until Nx do begin m:=p[i,ix]*p[j,ix];
              if m ≠0 then Ober[i,j]:=false
            end;
            for if:=1 step 1 until Nf do begin m:=pf[i,if]*pf[j,if]
              if m ≠ 0 then Ober[i,j]:=false end end;
          for i:=1 step 1 until Na do begin Nober[i]:=0;
            for j:=1 step 1 until Na do
              if Ober[i,j] then Nober[i]:=Nober[i]+1 end;

              input (60,'N',Npri);
          for i:=1 step 1 until Npri do
              input (60,'2(N)',prix[i,1],prix[i,2]);
              input (60,'2(N)',Ns,stegbyt);
          Rs:=0;

NYSA:     Rs:=Rs+1;
          if Rs > Ns then goto NYKO;
              output (61,'/');
              input (60,'N',Np);
          if Np < 0 then begin Np:=-Np; Pegas:=true; lna[Na+1]:=0; F:=1 end
            else Pegas:=false;
          Nva:=0; ia:=0; Titer:=false;

NYA:      ia:=ia+1
          if ia > Na then goto PLAN;
          Noll[ia]:=false; A0[ia]:=AT[ia]:=-99·99;
              input (60,'N',Hur[ia]);
          if Hur[ia] < 0 then begin Hur[ia]:=-Hur[ia]; Noll[ia]:=true end;
          if Hur[ia] < 5 then begin Nva:=Nva+1; iva[Nva]:=ia;
              input (60,'2(N)',start[ia],tol[ia]);
            lna[ia]:=start[ia] end;
          goto HURSA[Hur[ia]];

Hur1:         input (60,'N',Tot[ia]);
```

```
            output (61,'/,B,'TOT',ZD,'=',−D.4D10 +ZD',ia,Tot[ia]);
        goto NYA;
Hur2:       input (60,'2(N)',Tot[ia],step[ia]);
        goto NYA;
Hur3:   goto NYA;
Hur4:       input (60,'2(N)',A0[ia],AT[ia]);
        Titer:=true; goto NYA;
Hur5:       input (60,'N',w);
        lna[ia]:=w*ln10;
            output (61,'B,'LOGA',ZD,'=',−2ZD.3D',ia,w);
        goto NYA;
Hur6:       input (60,'N',w);
        lna[ia]:=w*ln10;
            input (60,'N',w);
        step[ia]:=w*ln10;
Hur7:   goto NYA;
PLAN:   m:=0;
        for i:=1 step 1 until (Nva−1) do begin
          if Nober[iva[i+1]] > Nober[iva[i]] then begin m:=iva[i];
            iva[i]:=iva[i+1]; iva[i+1]:=m end
          else begin if Mono[iva[i+1]] and not Mono[iva[i]] and Nober[iva[i+1]]=
            Nober[iva[i]] then begin m:=iva[i]; iva[i]:=iva[i+1];
            iva[i+1]:=m end end end;
        if m ≠0 then goto PLAN;
        iva[Nva+1]:=0;
        for Rva:=1 step 1 until Nva do begin ivar:=iva[Rva]; ivabra[ivar]:=
            iva[Rva+1]; i:=0;
HOPP:   i:=i+1;
        if Ober[ivar,iva[i]] then goto HOPP
            else ivanov[ivar]:=iva[i] end;
        if Pegas then begin
            input (60,'2(N)',Ptot,tolp);
            output (61,'/,B,'PTOT='3ZD.4D',Ptot)
        end;
        if Titer then begin
            input (60,'N',V0);
            output (61,'/,'TITER V0='3ZD.3D',V0);
            output (61,'/,B,'A0='');
        for ia:=1 step 1 until Na do
            output (61,'−ZD.5D',A0[ia]);
            output (61,'/,B,'AT='');
          for ia:=1 step 1 until Na do
            output (61,'−ZD.5D',AT[ia])
        end
        for j:=1 step 1 until Npri do begin ix:=prix[j,1]; m:=prix[j,2];
          if ix > 0 then begin skriv[j]:=ix;
            if m = 1 then tryn[j]:=1;
            if m = 2 then tryn[j]:=2;
            if m < 0 then begin ia:=−m; tryn[j]:=3; skriv[j]:=10*ix+ia end end;
          if ix = 0 and m =0 then begin tryn[j]:=11; skriv[j]:=0 end;
          if ix < 0 then begin ia:=−ix; skriv[j]:=ia; tryn[j]:=m+3;
            if m < 0 then begin m:=−m; tryn[j]:=12; skriv[j]:=10*ia+m end end end;
            output (61,'/');
        j:=0;
```

```
MERTRYCK: j:=j+1;
          if j > Npri then goto SLUTTRYCK;
             else goto TRYCKA[tryn[j]];

Tryck1:  output (61,"          C"); goto Skrivj;
Tryck2:  output (61,"   LOG C"); goto Skrivj;
Tryck3:  output (61," PC/TOT"); goto Skrivj;
Tryck4:  output (61,"          A"); goto Skrivj;
Tryck5:  output (61,"   LOG A"); goto Skrivj;
Tryck6:  output (61,"LG(TO/A)"); goto Skrivj;
Tryck7:  output (61,"      TOT"); goto Skrivj;
Tryck8:  output (61,"   A/TOT"); goto Skrivj;
Tryck9:  output (61,"   LOGD"); goto Skrivj;
Tryck10: output (61," D/(1+D)"); goto Skrivj;
Tryck11: output (61,"        VT"); goto Skrivj;
Tryck12: output (61," (T-A)/T"); goto Skrivj;
SKRIVJ:  output (61,'3Z',skriv[j]);  goto MERTRYCK;

SLUTTRYCK: Rp:=0;
NYP:       Rp:=Rp+1;
           if Rp > Np then goto NYSA;
           ia:=0; Nut:=0; Singfall:=false;
           if Pegas then Karl[Na+1]:=1;
           if Titer then begin
              input (60,'N',VT);
             Vtot:=V0+VT end;

Nya1:      ia:=ia+1;
           if ia > Na then goto SLINGOR;
           if Pegas and Hur [ia] < 3 and Rp > 1 then Tot[ia]:=Ntot[ia];
           goto PBER[Hur[ia]];

Nya2:      if Mono[ia] and Tot[ia] ≤ 0 then Tot[ia]:=1_10-12;
           if Pegas then Ntot[ia]:=Tot[ia];
           goto Nya1;

Pber1:     goto Nya2;
Pber2:     if Rp ≠ 1 then Tot[ia]:=Tot[ia]+step[ia];
           goto Nya2;

Pber3:        input (60,'N',Tot[ia]);
           goto Nya2;
Pber4:     Tot[ia]:=(A0[ia]*V0+AT[ia]*VT)/Vtot; goto Nya2;
Pber5:     goto Nya1;
Pber6:     if Rp ≠ 1 then lna[ia]:=lna[ia]+step[ia];
           goto Nya1;
Pber7:        input (60,'N',w);
           lna[ia]:=w*ln10; goto Nya1;

SLINGOR:   for Rva:=1 step 1 until Nva do begin i:=iva [Rva];
             if Pegas then Tot[ia]:=F*Ntot[ia];
             if tol[ia] > 0 then toly[ia]:=tol[ia] else toly[ia]:=abs(tol[ia]*Tot[ia]);
             Karl[ia]:=1 end;
           ivar:=iva[1];
           if Nfall > 0 then Lnaber;
           Lnbas;
           if Ber[ivar] then begin Cber; goto PROV end;

TJAT:      lna[ivar]:=x;
           if ivar > Na then begin F:=exp(x); goto SLINGOR end;
```

```
            if Falla[ivar] then begin Lnaber; Lnbas end;
            if ivar ≠ ivanov[ivar] then begin ivar:=ivanov[ivar]; Lnbas;
              if Ber[ivar] then begin Cber; goto PROV end end;
            Cber; Totber;
            goto ADA[Karl[ivar]];
PROV:       ivar:=ivabra[ivar];
            if ivar = 0 then goto FALLPROV;
            if Ber[ivar] then goto PROV;
            Totber;
            Lnbas;
            goto ADA[Karl[ivar]];

Ada1:       if y > y0 then begin Karl[ivar]:=3; x:=x-2 end
              else begin Karl[ivar]:=2; x:=x+2 end;
            steg[ivar]:=1; goto TJAT;

Ada2:       if y > y0 then begin Karl[ivar]:=4; x:=x-steg[ivar] end
              else x:=x+2;
            goto TJAT;

Ada3:       if y > y0 then x:=x-2
              else begin Karl[ivar]:=4; x:=x+steg[ivar] end;
            goto TJAT;

Ada4:       steg[ivar]:=0·5*steg[ivar];
            if steg[ivar] < stegbyt then goto Byt;
            if y > y0 then x:=x-steg[ivar] else x:=x+steg[ivar];
            goto TJAT;

Ada5:       if y > y0 then goto Byt;
            y1[ivar]:=y; Karl[ivar]:=7; goto KORDA;

Ada6:       if y > y0 then begin y2[ivar]:=y; Karl[ivar]:=7; goto KORDA end;
            goto BYT;

Ada7:       if y > y0 then begin x2[ivar]:=x; y2[ivar]:=y end
            else begin x1[ivar]:=x; y1[ivar]:=y end;

Korda:      w:=(x2[ivar]-x1[ivar])/(y2[ivar]-y1[ivar]); x:=x1[ivar]+w*(y0-y1[ivar]);
              goto TJAT;

Byt:        if y > y0 then begin x2[ivar]:=x; y2[ivar]:=y; x:=x-steg[ivar];
              x1[ivar]:=x; Karl[ivar]:=5 end
              else begin x1[ivar]:=x; y1[ivar]:=y; x:=x+steg[ivar]; x2[ivar]:=x;
              Karl[ivar]:=6 end;
            goto TJAT;

FALLPROV:   if Nf=0 then goto NOG;
            Bra:=true; Nyfall:=0;
            for if:=1 step 1 until Nf do
              if not Fall[if] then begin w:=0;
                for ia:=1 step 1 until Na do w:=w+lna[ia]*pf[ia,if];
                if w > lnKf[if] then begin Fall[if]:=true; Nyfall:=Nyfall+1;
                ifall[Nfall+Nyfall]:=if; Bra:=false end end;
            for i:=1 step 1 until Nfall do begin ia:=ibe[i]; w:=Tot[ia];
              if not Noll[ia] then w:=w-exp(lna[ia]);
              for ix:=1 step 1 until Nx do w:=w-p[ia,ix]*c[ix]; Totbe[i]:=w end;
            for i:=1 step 1 until Nfall do begin w:=0;
              for j:=1 step 1 until Nfall do w:=w+ruta[i,j]*Totbe[j];
              if w < 0 then begin Fall[ifall[i]]:=false; Bra:=false end end;
            if Bra then goto NOG;

INFALL:     Nfall:=Nfall+Nyfall;
            for ia:=1 step 1 until Na do Falla[ia]:=false;
            for i:=1 step 1 until Nfall do begin if:=ifall[i];
              if Fall[if] then begin
```

```
        for ia:=1 step 1 until Na do
        if pf[ia,if] ≠ 0 then Falla[ia]:=true end
      else begin Nfall:=Nfall−1;
        for j:=i step 1 until Nfall do ifall[j]:=ifall[j+1]; i:=i−1 end end;
    if Nfall = 0 then goto ANFALL;

BEFALL: for i:=1 step 1 until Nfall do iber[i]:=i;
    iber[Nfall+1]:=0;

UTFALL: for i:=1 step 1 until Nfall do begin ia:=iva[iber[i]];
      for j:=1 step 1 until Nfall do begin if:=ifall[j]; ruta[i,j]:=pf
        [ia,if] end end;
    Invert(Nfall,ruta,1₁₀−35,det,SING); goto ANFALL;

SING:   if not Singfall then begin
    for i:=1 step 1 until Nfall do ifspar[i]:=ifall[i];
      Nfspar:=Nfall; Nut:=0 end;
    i:=0; Singfall:=true;

HOPPSI: i:=i+1;
    if iber[i] = Nva then goto FUTT;
    if iber[i+1]=(iber[i]+1) then goto HOPPSI;
    iber[i]:=iber[i]+1; for j:=1 step 1 until (i−1) do iber[j]:=j;
    goto UTFALL;

FUTT:   if Nut=0 then goto UPPNUT;
    i:=0;

HOPPFUT: i:=i+1;
    if Fut[i]=Nfspar then goto UPPNUT;
    if Fut(i+1) = Fut[i]+1 then goto HOPPFUT;
    Fut[i]:=Fut[i]+1; for j:=1 step 1 until (i−1) do Fut[j]:=j;

INFUT:  for i:=1 step 1 until Nfspar do Fall[ifspar[i]]:=true;
    for i:=1 step 1 until Nut do Fall[ifspar[i]]]:=false;
    j:=0;
    for i:=1 step 1 until Nfspar do begin if:=ifspar[i];
      if Fall[if] then begin j:=j+1; ifall[j]:=if end end;
    goto BEFALL;

UPPNUT: Nut:=Nut+1; Nfall:=Nfspar − Nut;
    if Nfall < 0 then begin output (61, "TJI");
      goto Nyp end;
    for i:=1 step 1 until Nut do Fut[i]:=i; Fut[Nut+1]:=0; goto INFUT;

ANFALL: for ia:=1 step 1 until Na do Ber[ia]:=false;
    for i:=1 step 1 until Nfall do begin ia:=ibe[i]:=iva[iber[i]];
        Ber[ia]:=true end;
    Nvaf:=0;
    for i:=1 step 1 until Nva do begin ia:=iva[i];
      if not Ber[ia] then begin Nvaf:=Nvaf+1; ivaf[Nvaf]:=ia end end;
    for i:=1 step 1 until Nvaf do for j:=1 step 1 until Nfall do begin
      w:=0;
      for m:=1 step 1 until Nfall do
        w:=w+pf[ivaf[i],ifall[m]]*ruta[m,j]; rut1[i,j]:=w end;
    for i:=1 step 1 until Nvaf do for ix:=1 step 1 until Nx do
      begin ia:=ivaf[i]; w:=p[ia,ix];
      for m:=1 step 1 until Nfall do w:=w−rut1[i,m]*p[ibe[m],ix];
        pva[ia,ix]:=w end;
    goto SLINGOR;

NOG:    if Pegas then Sump;
    for ia = 1 step 1 until Na do
```

```
      if Hur[ia] > 4 then begin Tot[ia]:=if Noll[ia] then 0 else exp(lna[ia]);
    for ix:=1 step 1 until Nx do Tot[ia]:=Tot[ia]+p[ia,ix]*c[ix] end;
    for j:=1 step 1 until Npri do begin ix:=prix[j,1]; m:=prix[j,2];
    if ix > 0 then begin
      if m = 1 then skriv[j]:=c[ix];
      if m = 2 then begin
        if c[ix] > 0 then skriv[j]:=ln(c[ix])/ln10
        else begin w:=lnbeta[ix]; for ia:=1 step 1 until Na do w:=w+lna[ia]*
          p[ia,ix]; skriv[j]:=w/ln10 end end;
      if m < 0 then begin ia:=-m; skriv[j]:=p[ia,ix]*c[ix]/Tot[ia] end end;
    if ix=0 then skriv[j]:=VT;
    if ix < 0 then begin ia:=-ix; w:=exp(lna[ia]);
      if m = 1 then skriv[j]:=w;
      if m = 2 then skriv[j]:=lna[ia]/ln10;
      if m = 3 then skriv[j]:=(ln(Tot[ia])-lna[ia])/ln10;
      if m = 4 then skriv[j]:=Tot[ia];
      if m = 5 then skriv[j]:=w/Tot[ia];
      if m = 6 or m = 7 then begin
    if Kifas2[ia] then w1:=w else w1:=0;
    for ix:=1 step 1 until Nx do if ifas2[ix] then w1:=w1+p[ia,ix]*c[ix];
    w:=Tot[ia]-w1; y:=w1/w;
    if m = 6 then skriv[j]:=ln(y)/ln10 else skriv(j):=y/(1+y) end;
    if m < 0 then begin m:=-m; w:=0;
    for ix:=1 step 1 until Nx do if p[m,ix] ≠ 0 then w:=w+p[ia,ix]*c[ix];
      skriv[j]:=w/Tot[m] end
    end end;
        output (61,'/');
    for j:=1 step 1 until Npri do
        output (61,'-2ZD.6D',skriv[j])
    if Nf > 0 then begin
      if Nfall = 0 then
        output(61,"EJ FALL")
      else begin
        output(61," FALL");
      for i:=1 step 1 until Nfall do
        output(61,'2ZD', ifall[i])
    end end;
    goto NYP;
SLUT: end HALTAFALL;
```

TABLE II.—EXPLANATIONS OF SYMBOLS IN HALTAFALL (TABLE I)

real

det = determinant in Invert; *F* = factor for conversion from n_{ia}(*Ntot*[*ia*]) to T_{ia} (*Tot*) (8); *kbas* = factor in K_{ix} (or K_{if}) = *kbas*$*10^{pot}$; *lnc* = $\ln c_{ix}$; *ln*10=ln 10; *Ptot* = total gas pressure (9); *stegbyt* = see "input,III:1"; *tolp* = tolerance in solving (9) for *Ptot*; *VO* = original volume in titration; *VT* = added volume in titration; *Vtot* = total volume in titration; *x* = independent variable in $y(x)=y_0$(ADA); *y* = dependent variable; *y*0 = value for *y* aimed at in $y(x)=y_0$; *w*, *w1* = numerical values in general.

integer (nr = number)

i = integer in general; *ia* = serial nr of component A_{ia} (1→*Na*); *if* = serial nr of solid F_{if} (1→*Nf*); *ivar* = *ia* nr of component for which T_{ivar} (5) is being tested, and a_{ivar} adjusted (varied); *ix* = serial nr of complex X_{ix} (1→*Nx*); *j*,*m* = integer in general; *Na* = nr of components; *Nf* = nr of possible solid phases; *Nfall* = nr of solids present at equilibrium; *Nfspar* = nr of solids indicated at FALLPROV; *Np* = nr of points in group treated; *Npri* = nr of printing orders; *Ns* = nr of groups; *Nut* = nr of solids systematically eliminated at some stage while *Singfall* is **true**; *Nva* = nr of equations for T_{ivar} to be tested (a_{ivar} to be varied) in absence of solids; *Nvaf* = nr of equations to be tested in presence of solids (13); *Nx* = nr of complexes; *Nyfall* = number of new solids indicated at FALLPROV; *pot* = exponent in K_{ix} = *kbas*$*10^{pot}$; *Rp* = serial number of point treated; *Rs* serial nr of group treated; *Rva* = serial number of *iva*[*Rva*] treated.

Boolean

Bra = **true** if equation fulfilled within tolerance limits, or solution found consistent in FALLPROV; *Fas2* = **true** if second fluid phase exists; *Pegas* = **true** if gas at constant pressure is treated; *Singfall* = **true** if the first matrix $\mathbf{pf}_{be}$ tried has come out singular.
Titer = **true** if titration is treated.

arrays

usually *ia* can have values from 1 to *Na*, *if* from 1 to *Nf*, *ix* from 1 to *Nx*, *ivar* from *iva*[1] to *iva*[*Nva*+1]. Dimensions are given only where important and not obvious.
AO[*ia*], *AT*[*ia*] = total concentration of A_{ia} in original and added solutions at titration; *lna*[*ia*] = natural logarithm of activity a_{ia} of component A_{ia} (2); *Ntot*[*ia*] = number of moles of A_{ia} in portion considered, if *Pegas* (8); *start*[*ia*] = first guess for *lna*[*ia*] in solving (5); *steg*[*ia*] = step for adjusting *lna*[*ia*] in ADA; *step*[*ia*] = spacing between constant ln a_{ia} or *Tot*[*ia*] values to be considered; *tol*[*ia*] = *toly*[*ia*] = tolerance input (see input III:2), and absolute tolerance in solving equation (5) or (16) for *Tot*[*ia*]; *Tot*[*ia*] = T_{ia}, total concentration of component A_{ia} (5); *Totbe*[*i*] = term for *ia*=*ibe*[*i*] in $T_{be} - a_{be} - p_{be} * c$ [equation (15)], used for calculating *cf* (after FALLPROV); *Totmi*[*i*] = term in $T_{ia} - a_{ia}$ (or T_{ia}, if *Noll*[*ia*]) where *ia*=*ibe*[*i*], *i*=1→*Nfall* (Lnaber); *Totva*[*ia*] = term in T_{vaf} reduced total concentration in presence of solids (16*a*, Lnaber); *x1*[*ia*], *x2*[*ia*] = values for *x* below and above right value in ADA; *y1*[*ia*], *y2*[*ia*] = values for *y* corresponding to *x*1 and *x*2; *lnKf*[*if*] = ln *Kf*, where *Kf* = equilibrium constant for dissolution of solid F_{if} to form components (11); *lnKmi*[*if*] = term in **lnKf′**, reduced ln*Kf* (14*a*, Lnaber).
pf[*ia*,*if*] = number of formula units of component A_{ia} in formula unit of solid F_{if} (10); *p*[*ia*,*ix*] = number of formula units of component A_{ia} in complex X_{ix} (1); *pva*[*ia*,*ix*] = term in $\mathbf{p}'_{vaf}$, reduced **p** (16*b*, ANFALL); *ruta*[*i*,*j*] = term in $\mathbf{pf}_{be}^{-1}$ (11m′; 14,15, UTFALL); *rut1*[*i*,*j*] = term in $\mathbf{pf}_{vaf} * \mathbf{pf}_{be}^{-1}$ (16*a*,16*b*,ANFALL); *skriv*[*j*] = *j*'th quantity to be printed;
c[*ix*] = concentration of complex X_{ix} (3); *lnba*[*ix*] = part of ln(*c*[*ix*]) independent of *lna*[*ivar*] (4, Lnbas); *lnbeta*[*ix*] = ln K_{ix} where K_{ix} is the equilibrium constant for formation of complex X_{ix} from components (4).

Integer array

Fut[*i*] = *ifspar* number of *i*'th solid to be eliminated at some stage in systematic variation during *Singfall*; *Hur*[*ia*] = number characterizing type of information given on T_{ia} or lna_{ia} (input III:2); *ibe*[*m*] = *ia* number for m'th a_{ia} to be calculated by means of (14) (*m* = 1→*Nfall*); *iber*[*j*] = *j*'th of *iva* numbers to be an *ibe* (*ibe*[*j*] = *iva*[*iber*[*j*]]), *j* = 1→*Nfall*; *ifall*[*m*] = *if* number of *m*'th solid F_{if} present at equilibrium, *m*=1→*Nfall*; *ifspar*[*m*] = *if* number of *m*'th solid indicated as possible after FALLPROV (saved during Singfall); *iva*[*m*] = *ia* number for *m*'th T_{ia} to be tested in absence of solids (*m*=1→N_{va}); *ivabra*[*ivar*] = *ivar* to be tested after *ivar*, if (5) [or (16)] is satisfied (*Bra* **true**); *ivaf*[*m*] = *ia* number for *m*'th T_{ia} to be tested in presence of solids (*m*=1→N_{vaf}); *ivanov*[*ivar*] = *ia* to be tested after *ivar*, if equation (5) [or (16)] is not satisfied; *Karl*[*ia*] = control number for solving the equations (5) [or (16)] using switch ADA[*Karl*]; *Nober*[*ia*] = number of other components, which are independent of A_{ia} (compare Boolean array *Ober*); *prix*[*l*→N_{pri},1→2]=number indicating printing orders; *tryn*[*j*] = number indicating heading of *j*'th column in output table.

Boolean array

Ber[*ia*] = **true** if *lna*[*ia*] is calculated by means of (14); *Fall*[*if*] = **true** if F_{if} is assumed present at equilibrium; *Falla*[*ia*] = **true** if A_{ia} is assumed to occur in one or more solids at equilibrium; *Kifas2*[*ia*] = **true** if component A_{ia} is defined so that its a_{ia} = [A_{ia}] in the second phase; *Mono*[*ia*] = **true** if A_{ia} only takes part in mononuclear complexes (*p*[*ia*,*ix*]=0 or 1 for all *ix*); *Noll*[*ia*] = **true** if a_{ia} does not give a concentration term in T_{ia} (5); *ifas2*[*ix*] = **true** if complex X_{ix} occurs in the second phase; *Ober*[*i*,*j*] = **true** if a_i and a_j are "independent" (no complex or solid contains both A_i and A_j, hence *p*[*i*,*ix*]∗*p*[*j*,*ix*] =0 for all *ix*, and *pf*[*i*,*if*]∗*pf*[*j*,*if*]=0 for all *if*).

TABLE III.—EXAMPLES OF INPUT FOR HALTAFALL. EXPLANATIONS WITHIN PARANTHESES ARE, OF COURSE, NOT GIVEN AS INPUT

(3*a*) Components: Cu^{2+}, H^+, NH_3. Complexes: $Cu(NH_3)_n^{2+}$ (*n*=1,2,3,4,5), NH_4^+, OH^-, Solids: none. Printing orders: the log a_{ia} for Cu^{2+} and H^+, c_{ix} for $Cu(NH_3)_n^{2+}$ with *n*=0,1,2,3,4,5.
Group 1: $[Cu]_{tot}$ = 0·1*M*, $[NH_3]_{tot}$ = 0·5*M*, log $[H^+]$ varied from −11 to −1·5 in steps of 0·5.
Group 2: Titration. To 50 ml of solution with 0·10*M* Cu^{2+}, 0*M* excess of H^+ and 0·5*M* NH_3, increasing amounts of solution with 0*M* Cu^{2+}, 0*M* NH_3 and 1·0*M* H^+ are added.

```
   Input:
(0:1) 0, 0,/NH3, H+, Cu(II)/
(I:1,I:2)  3(Na), 7(Nx),
           1·0, −14, 0, −1, 0, (OH−) 4·0, 9, 1, 1, 0, (NH4+)
           2·04, 4, 1, 0, 1, (CuNH3 2+) 9·55, 7, 2, 0, 1, (Cu(NH3)2 2+)
           1·05, 11, 3, 0, 1, (Cu(NH3)3 2+) 2·09, 13, 4, 0, 1, (Cu(NH3)4 2+)
           6·30, 12, 5, 0, 1, (Cu(NH3)5 2+)
(I:3)      0(Nf, no solid),
(II)       10(Npri), −2, 2, −1, 2, −3, 2, −1, −3, −2, 4,
           2,1, 2,2, 6,−3, −3,−3, −3,5, (print log a2 = log[H+], log a1,
           log a3, NH3 per Cu, [H+]tot, etc.)
(III:1)    2(Ns), 0·4(stegbyt),
(III:2,
  group 1)20(Np1),
           1, −2, 1 10–5, 0·5, (hur, start, tol, Tot for NH3) 6, −11·0, 0·5,
           (hur, 1st log a ta, step, for H+) 1, −4, 1 10–6, 0·1, (hur, start,
           tol, Tot for Cu2+)
(III:2,
  group 2)20(Np2),
           4, −2, 1 10–5, 0·5, 0, 4, −20, 1 10–5, 0, 1·0, 4, −4, 1 10–6,
           0·1, 0, (hur, start, tol, A0, AT for NH3, H+, Cu2+)
(III:3)    100(V0), 2, 4, 6, . . . . . , 100(VT),
(O:2)      −1, −1,
First output line (group 1):
LOG A2  LOG A1  LOG A3  (T−A)/T13 TOT2     C2         LOG C2
−11·0000 −1·0081  −10·3218 3·9791     0·002926 0·003926  −2·4060
   PC/TOT63  LG(TO/A)3  A/TOT3
...
   0·9249      9·3218      0·00000
```

(3*b*) Components: Ag^+, I^-. Complexes: $AgI_n^{(n-1)-}$, with n=1,2,3,4,
Solid: AgI. Printing orders: V_T, log a_{ta} for Ag^+ and I^-, log c_{ta} for the four complexes.
Group 1: Titration. To 100 ml of solution with 0·1*M* Ag^+, 0*M* I^-, increasing amounts of solution with 5·0*M* I^-, 0*M* Ag^+ are added.

```
   Input: (0:1):0,0, (SILVERJON JODIDJON)
(I:1,I:2)  2(Na), 4(Nx),
           1·2, 8, 1, 1, (AgI) 1·0, 11, 1, 2, (AgI2−) 5·0, 13, 1, 3, (AgI3 2−) 2·5, 14, 1, 4, (AgI4 3−)
(I:3)      1(Nf)
           4·0, −17, 1·0, 1·0, (AgI(s))
(II)       7(Npri), 0,0, −1,2, −2,2, 1,2, 2,2, 3,2, 4,2, (print orders)
(III:1)    1(Ns), 0·4(stegbyt),
(III:2)    13(Np1),
           4, −1, 1 10–6, 0·1, 0, (hur . . . Ag+) 4, −10, 1 10–6, 0, 5·0, (hur . . . I−)
(III:3)    100(V0), 5, 10, . . . 100, (VT)
(0:2)      −1, −1,
First output line:
VT   LOG A1   LOG A2  LOG C1  LOG C2  LOG C3  LOG C4
5·000 −15·5523  −0·8456  −8·3188  −6·2436  −4·3902  −4·5368  FALL1
```

(3*c*) Components: Ag^+, Cl^-, Br^-, I^-, H^+. Complexes: OH^-. Solids: AgCl, AgBr, AgI, AgI′ (metastable), Ag_2O (AgH_{-1}). Printing orders: *VT*, log a_{ta} for Ag^+, Cl^-, Br^-, I^-, and H^+; c_{ta} for OH^-.
Group 1: Titration. To 50 ml of solution with 0*M* Ag^+, 0·01*M* Cl^-, 0·01*M* Br^-, 0·01*M* I^- and −0·02*M* H^+, increasing amounts of solution with 0·2*M* Ag^+, and 0*M* of the other reagents, are added.

```
   Input:
(I:1,I:2)  5(Na), 1(Nx),
           1·0, −14, 0, 0, 0, 0, −1, (OH−)
(I:3)      5(Nf),
           1·8, −10, 1, 1, 0, 0, 0, (AgCl) 4·6, −13, 1, 0, 1, 0, 0, (AgBr)
           4·0, −17, 1, 0, 0, 1, 0, (AgI) 8·3, −17, 1, 0, 0, 1, 0, (AgI′)
           2·0, 6, 1, 0, 0, 0, −1, (AgOH)
```

(II) 7(*Npri*), 0, 0, −1, 2, −2,2, −3,2, −4,2, −5,2, 1,2, (print orders)
(III:1) 1(*Ns*), 0·4(*stegbyt*),
(III:2) 30(*Np*),
4, −10, 1_{10}–5, 0, 0·2, (*hur* . . . Ag^+), 4, −4, 1_{10}–5, 0·01, 0,
4, −4, 1_{10}–5, 0·01, 0, (*hur* . . . Cl^-) 4, −4, 1_{10}–5, −0·02, 0,
(*hur* . . . H^+)
(III:3) 100(V_0), 1, 2, 3, . . . , 30, (V_T)
(0:2) −1, −1;

First output line:
VT LOG A1 LOG A2 LOG A3 LOG A4 LOG A5 LOG C1
1·000 −14·2965 −2·0043 −2·0045 −2·1014 −2·0045 −11·9955 FALL 3
(3*d*) Components: UO_2^{2+}, (H^+,) HA(=DBP), D(=TBP, in hexane). Complexes (all, except H_2A_2(aq), in the hexane phase): H_2A_2(aq); HA, HAD, HAD_2, $(HA)_2$, $(HA)_2D$, $(HA)_4$, $UO_2(HA)_4$, $UO_2(HA)_4D$, $UO_2(HA)_3D$, $UO_2(HA)_2D_2$, UO_2D_2, D.
Solids: none.
Group 1: $[UO_2]_{tot} = 1 \times 10^{-6} M$ (trace amounts), $[TBP]_{tot} = 0{\cdot}04M$; $[HA]_{tot}$ given for each point.
Printing orders: $[HA]_{tot}$, log a_{fa} for DBP and TBP, log D (UO_2^{2+}) and $D/(1+D)$.

Input:
(I:1,I:2) 4(*Na*), −13(*Nx*),
(I:2a) 0 ("*m*")
0, 0, 0, 2, 0, 0, (H_2A_2(aq)) 3·4977, −3, 0, 1, 0, 1, (HA)
3·0177, 0, 0, 1, 1, 1, (HAD) 9·1722, 0, 0, 1, 2, 1, (HAD_2)
5·5686, 1, 0, 2, 0, 1, ($(HA)_2$) 1·0444, 3, 0, 2, 1, 1, ($(HA)_2D$)
6·2410, 4, 0, 4, 0, 1, ($(HA)_4$) 2·0146, 9, 1, 4, 0, 1, ($UO_2(HA)_4$)
1·3481, 12, 1, 4, 1, 1, ($UO_2(HA)_4D$)
7·9818, 9, 1, 3, 1, 1, ($UO_2(HA)_3D$) 3·9200, 5, 1, 2, 2, 1,
($UO_2(HA)_2D_2$) 7·5065, −3, 1, 0, 2, 1, (UO_2D_2) 1·0, 0, 0, 0, 1, 1,
(D)
(I:3) 0(*Nf*),
(II) 5(*Npri*),
−2,4, −2,2, −3,2, −1,6, −1,7 (print orders),
(III:1) 3(*Ns*), 0·2 (*stegbyt*),
(III:2) 38(Np_1),
1, −20, -1_{10}–6, 1_{10}–6, (*hur* . . . UO_2^{2+}) 3, −10, -1_{10}–6, (*hur* . . . HA)
−1, −4, -1_{10}–6, 0·040, (*hur* . . . D)
(III:3) 0·50(Tot_2), 0·397(Tot_3), . . . (*etc.*) −1, −1;

First output line:
TOT 2 LOG A2 LOG A3 LOG D1 D/(1+D)1
0·5000 −1·4794 −1·7519 4·5025 0·999969
(3*e*) Components:[17] C(s), H_2(g), O_2(g). Complexes (all in gas phase): H_2O, CO, CO_2, CH_4, C_2H_4, C_2H_2. Solid: C(s). Printing orders: see output (partial pressures in atm).
Group 1: gas at constant pressure, 1·0 atm. Log $P(O_2)$ varies from −26·6 to −25·2 by steps of 0·2. Mole ratio $H_2/C = 16{\cdot}5/10$.

Input:
(I:1,I:2) 3(*Na*), 5(*Nx*),
1·95, 13, 0, 1, 0·5, (H_2O) 8·51, 11, 1, 0, 0·5, (CO)
6·67, 25, 1, 0, 1, (CO_2) 1·41, 0, 1, 2, 0, (CH_4)
4·27, −8, 2, 2, 0, (C_2H_4)
(I:3) 1(*Nf*),
1·0, 0, 1, 0, 0, (C(s))
(II) 7(*Npri*),
−3,2, −2,1, 1,1, 2,1, 3,1, 4,1, 5,1 (print orders)
(III:1) 1(*Ns*), 0·4(*stegbyt*),
(III:2) −8(Np_1),
−1, 0, 1_{10}–5, 10, (*hur* . . . C) 1, −20, 1_{10}–5, 16·5 (*hur* . . . H_2), 6, −26.6,
0·2 (*hur* . . . O_2)
1(*ptot*), 0·001(*tolp*),

(0:2) −1, −1;

First output line:

LOG A 3 A2 C1 C2 C3 C4 C5
−26·6000 0·324252 0·316896 0·042651 0·167375 0·148526 0·000000 FALL 1

(3*f*) Components:[17] C(s), H_2(g), O_2(g), S_2(g), Ca(s). Complexes (all in gas phase): H_2O, CO, CO_2, CH_4, H_2S, COS, SO_2, SO_3, Ca(g). Solids: C, $CaCO_3$, CaO, CaS, $CaSO_4$. Printing orders: log a_{ia} for O_2, c_{ia} for H_2O, CO, CO_2, CH_4, H_2S, COS, SO_2, SO_3, a_{ia} for S_2 (=partial pressures in atm).

Group 1: constant gas pressure = 1·0 atm, mole ratio C/H_2/S/Ca=10/16·25/0·6/0·3, log $P(O_2)$ varied from −35 to −3 in steps of 1.

Input:

(I:1,I:2) 5(*Na*), 9(*Nx*),
1·95, 13, 0, 1, 0·5, 0,0, (H_2O) 8·51, 11, 1, 0, 0·5, 0, 0, (CO)
6·67, 25, 1, 0, 1, 0, 0, (CO_2) 1,41, 0, 1, 2, 0, 0, 0, (CH_4)
2·04, 3, 0, 1, 0, 0·5, 0, (H_2S) 9·55, 13, 1, 0, 0·5, 0·5, 0, (COS)
6·61, 19, 0, 0, 1, 0·5, 0, (SO_2) 2·09, 21, 0, 0, 1·5, 0·5, 0, (SO_3)
1·70, −6, 0, 0, 0, 1, (Ca)

(I:3) 5(*Nf*)
1·0, 0, 1, 0, 0, 0, 0, (C) 5·0, −66, 1, 0, 1·5, 0, 1, ($CaCO_3$)
7·94, −37, 0, 0, 0·5, 0, 1, (CaO) 7·75, −31, 0, 0, 0, 0·5, 1,
(CaS) 6·02, −75, 0, 0, 2, 0·5, 1, ($CaSO_4$)

(II) 10(*Npri*),
−3,2, 1,1, 2,1, 3,1, 4,1, 5,1, 6,1, 7,1, 8,1, −4,1 (print orders)

(III:1) 1(*Ns*), 0·4(*stegbyt*)

(III:2) −33(*Np*$_1$), −1, 0, 1_{10}–5, 10 (*hur* . . . C) 1, −20, 1_{10}–5, 16·25
(*hur* . . . H_2) 6, −35, 1·0, (*hur* . . . O_2) 1, −20, 1_{10}–5, 0·3,
(*hur* . . . S_2) −1, −20, 1_{10}–5, 0·3, (*hur* . . . Ca)
1(*ptot*), 0·001(*tolp*),

(0:2) −1,−1;

First output line:

LOG A 3 C1 C2 C3 C4 C5 C6
−35·000 0·000034 0·000003 0·000000 0·424572 0·026248 0·000000
. . . C7 C8 A4
0·000000 0·000000 0·000000 FALL 1 4
(For log $P(O_2)$ −35 to −27:solids 1 and 4 (C(s) and CaS(s))
For log $P(O_2)$ −26 to −22:solid 2 ($CaCO_3$)
For log $P(O_2)$ −21 to −3:solid 5 ($CaSO_4$))

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Zusammenfassung—Das Rechenprogramm HALTAFALL wird beschrieben, das die Gleichgewichtskonzentrationen der Spezies in Gemischen aus jeder Zahl von Komponenten berechnet, die jede Anzahl von Komplexen und festen Reaktionsprodukten bilden können, sofern bei den Gleichgewichtsberechnungen Konzentrationen (oder Partialdrucke) benutzt werden können. Selbstverständlich müssen die Gleichgewichtskonstanten und genügend Daten über die analytische Zusammensetzung bekannt sein. Auf einige Anwendungen wird hingewiesen. Die flexiblen Eingangsregeln machen seine Anwendung auf ein breites Spektrum von Fragestellungen möglich. Aus der eingegebenen Information ermittelt das Programm selbst einen wirksamen Plan zur

Lösung der simultanen Gleichungen. Das Programm enthält auch die Möglichkeit, herauszufinden, welche unter vielen möglichen festen Phasen in einer gegebenen Gleichgewichtsmischung wirklich erscheint.

Résumé—On décrit un programme de computation, HALTAFALL, qui calcule les concentrations à l'équilibre des espèces dans des mélanges à n'importe quel nombre de composants, qui peuvent former n'importe quel nombre de complexes et de phases solides, en admettant qu'on peut utiliser les concentrations (ou les pressions partielles) dans les calculs d'équilibre. Evidemment, les constantes d'équilibre doivent être connues et l'on doit fournir suffisamment de données sur la composition brute. On indique quelques applications. Les règles souples d'admission le rendent applicable à des problèmes variés. A partir de l'information de départ, le programme lui-même établit un plan convenable pour la résolution des équations simultanées. Le programme fournit aussi un moyen efficace pour trouver laquelle des nombreuses phases solides possibles peut réellement apparaître dans un certain mélange en équilibre.

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DETERMINATION OF TRACES OF ORGANIC FLUORINE IN HYDROCARBONS*

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Summary—Organic samples containing down to 0·2 ppm of fluorine may be analysed by first converting the organic fluorine into inorganic fluoride by treatment with sodium biphenyl, followed by removal of diverse cations with a cation-exchanger before conductometric titration with lanthanum acetate. Effect of variables, sources of error, and control of reagent blanks are evaluated. For the 0·2–1 ppm organic fluorine level in synthetic blends made from 1-fluoronaphthalene, the relative estimated standard deviation was 7·8%; the mean relative error was 6·2%. Based on the mean range from duplicate analyses of catalytically processed samples in the C_{12} boiling range, at the 1 ppm fluorine level the estimated standard deviation was 0·087 ppm of fluorine. One analyst can determine the fluorine content of about 12 samples in 8 hr.

TRACES of organic fluorine can be produced in fluoride-catalysed petrochemical processes, and may adversely affect subsequent catalytic operations. Quality control may sometimes require determination of 1 ppm of fluoride.

Determination of traces of organic fluorine generally requires conversion of the fluorine in a large hydrocarbon sample into inorganic fluoride, followed by separation and determination. This carbon-fluorine bond cleavage is normally accomplished either by oxidation of all organic matter, or by reductive cleavage.[1] Attempts to oxidize the sample and recover all the fluoride at these low levels by using a quartz Wickbold burner[2] resulted in low recoveries. Use of sodium biphenyl[3] to accomplish the cleavage for traces of bromides, iodides and chlorides has been described.[4,5] Liggett[6] has reported the use of sodium biphenyl for reductive cleavage of organic fluorides where the organic fluoride was the major constituent. The rapid cleavage at room-temperature and the commercial availability of the reagent make this approach for the conversion of organic fluorine into fluoride ion an attractive one for control work.

Once the organic fluoride has been cleaved, there are several methods for determination of traces of inorganic fluoride that might be applied.[7] Attempts to use spectrophotometric methods employing either thorium chloranilate[8] or SPADNS [4,5-dihydroxy-3-(*p*-sulphophenylazo)-2,7-naphthalenedisulphonic acid, trisodium salt][9] after the sodium biphenyl treatment and hydrolysis were not successful; the blanks and recoveries were erratic, and seemed to be affected by traces of organic material from the biphenyl reagent.

Dowdall[9] has compared conductometric methods for determining traces of

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fluoride and recommends titration of 200–500 μg of fluoride in 0·01*M* acetic acid with lanthanum acetate. Experimentation with various titrants in our laboratories corroborates his findings. Kubota[10] has described a conductometric lanthanum acetate method for determination of down to 0·095 mg of fluoride as hydrofluorosilicic acid, obtained by the Willard and Winter[11] distillation, with a relative standard deviation of 9%.

Because of the exploratory laboratory results, and the literature cited, attention was directed toward combining the sodium biphenyl treatment and the conductometric titration. In such an approach about 100 g of hydrocarbon sample containing about 0·5 ppm of organic fluorine would be taken, so that about 50 μg of inorganic fluoride would be available for titration.

EXPERIMENTAL

Apparatus

Titrator. Conductometric titrations were performed with a recording potentiograph (Metrohm, Model E 336) with conductometric titration attachment (Metrohm, Model E 365). An immersion cell (Type 608) with a cell constant of 0·695 cm^{-1} and a 1-ml gear-driven microburette were employed, and each chart-paper division corresponded to 10 μg of fluoride.

Cation-exchange column. A 1·5-cm diameter column, 10 cm long, was flanged out at the top into a reservoir 10 cm × 3·0 cm diameter and equipped with a Teflon stop-cock at the bottom. The column was filled with 50 ml of Dowex 50W-X8 resin supported on a cotton wad (glass wool is unsatisfactory and causes erratic recoveries) and prepared for use by washing with four equal portions of a mixture of 70 ml of water and 30 ml of concentrated hydrochloric acid, followed by washing with 400 ml of demineralized water.

Reagents

Sodium biphenyl in 15-ml vials, and fluorine-free toluene (Southwestern Analytical Chemicals, Austin, Texas).

Lanthanum acetate titrant (0·15*N* La^{3+}) was prepared by dissolving about 16 g of lanthanum acetate and 1 ml of glacial acetic acid in 700 ml of demineralized water, heating to boiling, cooling, filtering, adding 1 ml of glacial acetic acid, diluting to 1 l. with demineralized water, and standardizing against sodium fluoride by conductometric titration.

Procedure

Add three vials of sodium biphenyl slowly to 100 ml of toluene in a 500-ml separatory-funnel, rotating the funnel continuously during the addition. The stop-cock and stopper of the separatory-funnel should be lightly greased with a fluorine-free lubricant; Teflon stop-cocks cannot be used in this part of the procedure. Add 100–200 ml of sample, mixing continuously with a gentle swirling motion throughout the addition. Let the mixture stand in the stoppered funnel for 10 min. Add 15 ml of demineralized water, shake, vent the funnel while it is inverted, and draw off and collect the aqueous lower phase. Repeat this three times more. Boil the combined aqueous extracts in a Vycor beaker until traces of hydrocarbon are no longer evident. Cool the boiled extract and pass it through the ion-exchange column. Wash the column with four separate 25-ml portions of 50% aqueous ethanol, collecting the effluent and the washings in a tall-form 250-ml beaker. Purge the combined effluent and washings for about 15 min with nitrogen to remove carbon dioxide. Titrate conductometrically with 0·15*N* lanthanum, using a 1-ml microburette. Obtain a reagent blank by substituting for the sample a fluoride-free solvent of similar hydrocarbon type.

RESULTS AND DISCUSSION

Standardization

Sodium fluoride was dried at 110° for 2 hr, and dissolved to produce a solution containing 0·1000 mg of fluoride per ml. Aliquots of this solution were diluted with 1*M* sodium hydroxide to 50 ml, to give roughly the conditions obtained after hydrolysis of the sodium biphenyl used in the procedure. Neither this solution nor a portion

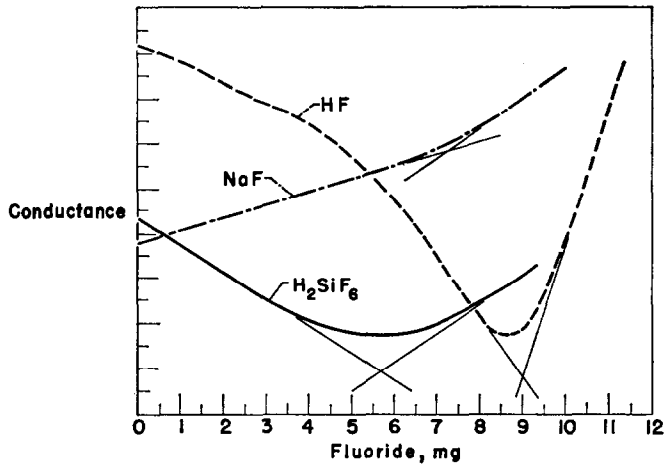

FIG. 1.—Conductometric end-points in presence of large amounts of sodium ions.

neutralized with acetic acid is suitable for titration directly, because the conductance of the large concentration of sodium ions causes an ill-defined end-point (Fig. 1). A satisfactory end-point is obtained with down to 1 mg of fluoride (Fig. 2) if the solution is neutralized by passing it through the cation-exchange column, and the carbon dioxide in the effluent and washings is removed by nitrogen stripping. The time required for removal of carbon dioxide by nitrogen stripping is determined experimentally (Table I), and for our apparatus was about 15 min. Recovery experiments showed that as little as 0·2 mg of fluoride may be determined conductometrically in this way, and that the estimated standard deviation is 0·007 mg for the range 0·2–1·0 mg (Table II).

Because the Willard and Winter distillation is commonly used to separate inorganic fluoride from many interfering substances, aliquots of standard hydrofluorosilicic acid were distilled to determine whether the conductometric titration could be used to titrate the fluoride present as SiF_6^{2-} in the distillate. The relative error for 0·1–0·4 mg of fluoride was 4%; for 0·5–1·0 mg of fluoride in the ion-exchange effluent, the relative

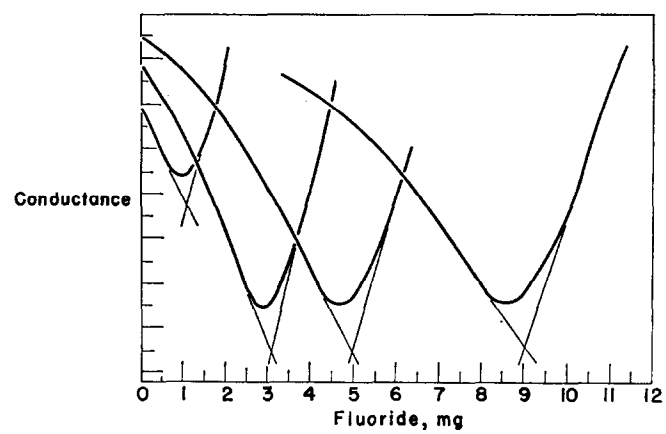

FIG. 2.—Conductometric end-points after removal of cations.

TABLE I.—DURATION OF NITROGEN STRIPPING REQUIRED FOR CO_2 REMOVAL

Stripping time, *min*	Fluoride added, *mg*	Fluoride found, *mg*
0	0·400	0·560
0	0·600	0·747
0	0·800	0·850
10	0·400	0·421
10	0·600	0·629
10	0·800	0·813
15	0·100	0·116
15	0·200	0·205
15	0·200	0·193
15	0·400	0·405
20	0·600	0·584
30	0·800	0·803

TABLE II.—RECOVERY OF FLUORIDE AFTER DIFFERENT PRETREATMENTS

Fluoride added, *mg*	Fluoride found, *mg*	
	Ion-exchange method	Willard and Winter distillation
0·100	0·116	0·106
0·200	0·193 0·197	0·210
	0·205 0·205	
0·300	—	0·308
0·400	0·396 0·405	0·410
0·500	—	0·498
0·600	0·600 0·606 0·593	0·602
0·700	—	0·706
0·800	0·804	0·804
0·900	—	0·900
1·00	0·998 0·984 0·990	1·006
	0·995 0·999 0·992	

TABLE III.—EFFECT OF RANDOM RESIN LEAKAGE INTO THE EFFLUENT

Fluoride added, *mg*	Fluoride found, *mg*
0·800	1·285
0·600	0·797
0·400	0·469
0·400	0·685
0·200	0·306

TABLE IV.—BLANK RELATIONSHIP TO BEAKERS USED

Beaker	Fluoride blank, *mg*
Vycor	0·336 0·344
Stainless steel	0·354 0·336
Nickel	0·354 0·347
Pyrex (normal stock)	0·634 0·562 0·590
Pyrex (new)	0·205 0·256
Pyrex (old)	0·815 0·977

error was 5% (Table II). Either the ion-exchange separation or the Willard and Winter distillation is therefore an acceptable pretreatment to the conductometric titration of fluoride. Irrespective of which pretreatment is used, if the temperature of the solution being titrated is allowed to drift more than $\pm 0{\cdot}5°$ during the titration, the end-point will be less clearly defined. Because of its simplicity, the ion-exchange separation was preferred. The column is regenerated with hydrochloric acid after each sample and washed with water, according to the procedure given for preparation of the column. Care must be taken to avoid any leakage of resin past the cotton plug support into the effluent, since the presence of even small amounts of resin in the titration vessel causes excessive titrant consumption (Table III). Before the sample

TABLE V.—ANALYSIS OF SYNTHETIC BLENDS*

Sample hydrocarbon type	Fluoride added, *μg*	Fluoride found, *μg*	Fluoride level, *ppm*
Iso-octane, 100 ml	99·8	115	1
Iso-octane, 100 ml	99·8	109	1
Iso-octane, 200 ml	99·8	102	0·5
Iso-octane, 200 ml	99·8	92·2	0·5
Iso-octane, 100 ml	49·9	51·0	0·5
Iso-octane, 100 ml	49·9	51·3	0·5
Iso-octane, 200 ml	49·9	52·0	0·25
Iso-octane, 200 ml	49·9	51·0	0·25
Dodecane, 200 ml	99·8	110	1

* Blank 410 μg of fluoride.

is passed through the column, any organic solvent left over from the extraction should be removed by boiling in a Vycor or metal beaker. The blanks from such beakers are reproducible whereas higher blanks are obtained if Pyrex is used, particularly if it is old and scratched, when the blanks are very variable, presumably due to leaching of fluoride from Pyrex by the alkali produced from the hydrolysis of the sodium biphenyl (Table IV).

In order to evaluate the proposed procedure, standard blends of 1-fluoronaphthalene in iso-octane and in n-dodecane were prepared. The 1-fluoronaphthalene

TABLE VI.—DUPLICATE ANALYSES OF DODECANE SAMPLES CONTAINING FLUORIDE FROM CATALYTIC PROCESSING

Sample No.	Trial 1, *ppm* F	Trial 2, *ppm* F	Range, *ppm* F
1	1·08	1·22	0·14
2	0·54	0·64	0·10
3	0·87	0·80	0·07
4	0·88	0·77	0·11
5	0·67	0·56	0·11
6	0·33	0·23	0·10

used was analysed by two independent methods and found to have a purity of 98·3%. For the 0·2–1·0 ppm organic fluorine level in the synthetic blends with 1-fluoronaphthalene (Table V), the relative estimated standard deviation was 7·8%; the mean relative error was 6·2%. From these data the method is judged to be able to determine $0{\cdot}2 \pm 0{\cdot}1$ ppm of fluorine. The estimated standard deviation calculated from the mean range of duplicate analyses of catalytically processed samples in the C_{12} boiling

range, at the 1-ppm fluorine level (Table VI), was 0·087 ppm of fluorine. One analyst can determine fluorine in about 12 samples in 8 hr.

It is expected that there will be very few serious interferences since either the Willard and Winter distillation or the ion-exchange separation will remove most of them. The main limitation to further improvement in detection limits results from the sodium biphenyl reagent blank. The conductometric titration is capable of quantitatively determining fluoride even at levels below 0·1 ppm.

Zusammenfassung—Organische Proben mit bis zu 0,2 ppm Fluor lassen sich analysieren durch Umwandeln des organischen Fluors in anorganisches durch Behandlung mit Diphenylnatrium, nachfolgende Entfernung verschiedener Kationen mit einem Kationenaustauscher und konduktometrische Titration mit Lanthanacetat. Der Einfluß variabler Größen, Fehlerquellen und Kontrolle der Blindwerte wurden verfolgt. Bei Testmischungen aus 1-Fluornaphthalin mit 0,2–1 ppm organischem Fluor war die relative Standardabweichung 7,8%, der mittlere relative Fehler 6,2%. Beruhend auf dem Mittelwert von Doppelanalysen katalytisch behandelter Proben im C_{12}-Siedebereich war die Standardabweichung im 1 ppm-Bereich 0,087 ppm Fluor. Ein Analytiker kann den Fluorgehalt von etwa 12 Proben in 8 Stunden bestimmen.

Résumé—On peut analyser des échantillons organiques contenant seulement 0,2 p.p.m. de fluor en transformant d'abord le fluor organique en fluorure inorganique par traitement au biphénylsodium, puis en éliminant divers cations par un échangeur de cations avant titrage conductimétrique à l'acétate de lanthane. On a estimé l'influence des variables, des sources d'erreurs et du contrôle des témoins de réactifs. Pour les teneurs 0,2–1 p.p.m. en fluor organique dans des mélanges synthétiques faits à partir du 1-fluoronaphtalène, l'écart type relatif estimé a été de 7,8%; l'erreur relative moyenne a été 6,2%. En se basant sur l'intervalle moyen à partir d'analyses en double d'échantillons réalisés catalytiquement dans le domaine d'ébullition C_{12}, à la teneur en fluor de 1 p.p.m., l'écart type estimé a été de 0,087 p.p.m. de fluor. Un analyste peut déterminer la teneur en fluor d'environ 12 échantillons en 8 h.

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SEPARATION AND ACID EQUILIBRIA OF XYLENOL ORANGE AND SEMI-XYLENOL ORANGE

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Summary—A mixture of Xylenol Orange (XO) and Semi-Xylenol Orange (SXO) was chromatographed on a cellulose column and ion-exchanged with Diaion SK-1 resin. XO and SXO in the acidic forms were titrated with sodium hydroxide to determine the basicities and the acid formation constants. The absorption spectra of XO and SXO were measured over a wide pH range, and were used for the calculation of acid formation constants, molar absorptivities, and the effect of ionic strength on the activity of XO. The purity of a commercial XO was measured by absorption spectroscopy, and it was found that the sample contained 36·3% of XO and 17·2% of SXO. Pure XO and SXO form a 1:2 and a 1:1 complex respectively with Zn(II). On the basis of these data the ionic structure of XO and SXO have been compared with those of Cresol Red and iminodiacetic acid, and discussed.

AS PART of an investigation on the chelates formed between sulphonphthalein derivatives and metal ions, the purification and some physico-chemical properties of Xylenol Orange (XO) and Semi-Xylenol Orange (SXO) were studied, and the structures were confirmed. Previous workers[1–3] have reported that XO has been synthesized from Cresol Red, iminodiacetic acid and formaldehyde by the Mannich condensation, and the structure was supposed to be 3,3′-bis[*N*,*N*′-di(carboxymethyl)aminomethyl]-*o*-cresolsulphonphthalein. So far as is known, however, the purification of this compound has never been successful, so that the mole ratio, suitable pH range, wavelength of maximum absorption, molar absorptivity and stability constant have been uncertain in the case of the chelate of XO and a metal ion such as Zr(IV),[4–7] Th(IV),[8,9] or Fe(III).[10–11]

Olson and Margerum have pointed out that SXO could be isolated from a mixture with XO by paper chromatography.[3] In the present work cellulose column chromatography and ion-exchange were used for separation of XO and SXO. The purity of XO and SXO separated by these methods was nearly 100% and the purity of each XO used in other work[4,8,12–23] could be evaluated by comparison of the data.

EXPERIMENTAL

Apparatus

A Toadenpa pH meter, Model HM-5A, was used. Standard buffer solutions (phthalate, phosphate, borate, 0·1*M* hydrochloric acid and 0·1*M* sodium hydroxide) were used for calibration.

All the absorption measurements were made with a Shimadzu Model SV-50AL spectrophotometer, with a 1-cm cell.

Toyo Roshi No. 52 paper was used for paper and cellulose column chromatography. Metals contained as impurity in the paper were almost all removed by developing with a hydrochloric acid–acetone solution. The cellulose column was prepared by shaking the paper with hot 1*M* nitric acid and packing the slurry.

Reagents

Sodium hydroxide solution, 0·1*M*. Carbonate free.

Buffer solutions. The following buffer solutions were used, adjusted to the value required.

pH 9·5–14: potassium hydroxide solution
pH 8–11: 1*M* ammonia–1*M* ammonium nitrate
pH 3–9·5: 1*M* veronal–1*M* acetic acid–1*M* potassium hydroxide
pH 3–6·5: 1*M* hexamine–1*M* nitric acid
pH 1–3: nitric acid
pH (H_0) 0·5: sulphuric acid

The reagents were analytical grade materials.

Synthesis of XO and SXO

These were synthesized by the Mannich condensation.[1-3] *o*-Cresol Red (1·91 g; 5×10^{-3} mole), 37% formaldehyde (1·00 ml; $1{\cdot}2 \times 10^{-2}$ mole), iminodiacetic acid (1·33 g; 1×10^{-2} mole), and sodium hydroxide (1 g) were dissolved in glacial acetic acid (50 ml). The mixture was heated at 63–65°. After 10 hr, the solvent was distilled off under reduced pressure.

Recrystallization from a polar solvent

Recrystallization of XO and SXO from alcohol, ketones, and esters was unsuccessful. From ethanol–sodium acetate solution, XO was precipitated, but part of it was decomposed to a red compound which formed no chelates with metal ions.

Separation by column chromatography and ion-exchange

The synthesized XO was chromatographed on alumina, silica gel, cation-exchange resin, and cellulose. On alumina and silica gel XO was decomposed, and from the ion-exchange resin a part of the XO could not be eluted. The mixture of XO and SXO was completely separated on a cellulose column by butanol saturated with 10% acetic acid. The elution order was: an unknown white compound, Cresol Red, sodium ions, SXO, XO, and iminodiacetic acid. The solvent was distilled off from each fraction under reduced pressure. The SXO and XO were the disodium and trisodium salt respectively. The SXO (1 g) was run through a column of Diaion SK-1 100-mesh cation-exchange resin (10–20 mequiv). The effluent solvent was distilled under reduced pressure and the residue was dried in a vacuum desiccator for two weeks. The compound was the free acid form of SXO, m.p. 201–204° (decomp.). Found: C, 57·6%; H, 5·0%; N, 2·6%; $C_{26}H_{25}O_9NS.H_2O$ requires: C, 57·24%; H, 4·99%; N, 2·57%.

The ion-exchange method used for XO containing sodium ions was virtually identical with that described for SXO, but the acid form of XO was again chromatographed and ion-exchanged to remove iminodiacetic acid completely. The product had m.p. 274–277° (decomp.). Found: C, 52·3%; H, 5·2%; N, 4·1%. $C_{31}H_{33}O_{18}N_2S.2H_2O$ requires: C, 52·54%; H, 5·11%; N, 3·95%.

Potentiometric titration

The acid form of XO (67·3 mg) was dissolved in 45 ml of water and 5 ml of 1*M* potassium nitrate, and the solution was titrated with 0·1*M* sodium hydroxide at 25 ± 0·1°, under nitrogen. Similar titrations were performed with the acid form of SXO and a commercial XO (Dotite XO).

Absorption spectra

To a 25-ml volumetric flask, 1 ml of 1–2·5 × 10^{-4}*M* XO or SXO solution, 0·5 ml of the buffer solution, and 2 ml of 1*M* potassium nitrate were added and diluted to the mark with water. The absorption spectrum of the solution was measured at room temperature. When the solution had only a small buffer action, it was measured under nitrogen so that the pH error might be below 0·03 within the range of pH 2–10.

RESULTS AND DISCUSSION

The synthesis and separation of XO and SXO

The removal of iminodiacetic acid and SXO from impure XO is difficult by means of recrystallization, and what is worse, iminodiacetic acid and SXO form chelates with many metal ions. Table I shows that XO is decomposed by methanol, ethanol and propanol and that the R_f value on a cellulose column is related to the number of

TABLE I. PAPER CHROMATOGRAPHY OF SYNTHESIZED XYLENOL ORANGE

No.	Developer	XO, R_f	SXO, R_f	Cresol Red, R_f	Other compounds, R_f
1	CH_3OH: 20% AcOH (4:1)	0–0·75	0·7–0·9	0·8–1·0	Purple decomp. product 0·8
2	C_2H_5OH: 20% AcOH (4:1)	0–0·95	0·9–1·0	0·9–1·0	Red decomp. product, 0·6 Purple decomp. product, 0·7
3	n-C_3H_7OH saturated with 20% AcOH	0·4–0·8	0·4–0·8	0·7–1·0	Red decomp. product, 0·4 Purple decomp. product, 0·6
4	n-C_4H_9OH saturated with 10% AcOH	0·05–0·1	0·6–0·8	0·8–1·0	Iminodiacetic acid, 0·03–0·07
5	n-C_4H_9OH saturated with 10% AcOH	0·3–0·5*	0·6–0·9*	0·8–1·0*	Iminodiacetic acid, 0·08–0·13
6	$CH_3COOC_2H_5$ saturated with 20% AcOH	0·5–0·75	0·7–0·95	0·9–1·0	

AcOH = acetic acid. When hydrochloric acid was used in place of acetic acid, the development was less perfect.

* Samples in the free acid form.

carboxyl groups in the molecule and to the number of sodium ions. Cresol Red and SXO were separated on a cellulose column from the sodium salts of XO, and XO and iminodiacetic acid were separated from the acid form of SXO. The purities of the products were established by elemental analysis, titration, paper chromatography, and absorption spectra.

SXO was easily synthesized at 55° with the theoretical amount of starting materials.

Calculation of acid formation constants from the pH titration curve

The acid formation constant is more suitable than the acid dissociation constant for discussion over a wide pH range. The constants are calculated by the methods of Bjerrum[24] and Block *et al.*[25] As the acid is of the H_NI type, then

$$H^+ + I^{N-} \rightleftharpoons HI^{(N-1)-},\ H^+ + HI^{(N-1)-} \rightleftharpoons H_2I^{(N-2)-},\ \ldots,\ H^+ + H_{(N-1)}I^- \rightleftharpoons H_NI \quad (1)$$

$$k_1 = [HI^{(N-1)}]/[H^+][I^{N-}],\ k_2 = [H_2I^{(N-2)-}]/[H^+][HI^{(N-1)-}],\ \ldots,\ k_N = [H_NI]/[H^+][H_{(N-1)}I^-] \quad (2)$$

$$C_S = \sum_{n=0}^{N} [H_nI^{(N-n)-}] \quad (3)$$

$$\bar{n} = C_H - [H^+] + [OH^-]/C_S = \sum_{n=1}^{N} J_nK_n \quad (4)$$

$$J_n = (n - \bar{n})[H^+]^n \quad (5)$$

C_S = Total concentration of the acid

C_H = Total concentration of protons

$\bar{n}$ = Mean number of protons in the acid

$k_1, k_2, \ldots, k_N$ = Acid formation constants

$K_n = k_1k_2 \ldots k_N$

$[H^+]$ is measured potentiometrically, C_S and C_H are calculated from the pH titration curve, and then the acid formation constants are calculated from equations (4) and (5). The concentration of free protons is corrected for the activity coefficient, which is measured by pH titration of nitric acid under the same conditions.

The pH titration curves of XO and SXO are shown in Fig. 1. The curves show the acid forms of XO and SXO to be H_6XO and H_4SXO as might be expected. Within the titration range 0–3 ml, the equilibria of XO are those of a strong acid corresponding to H_3I. From equations (3) and (4), an initial value of 1·092 was obtained for $\bar{n}$

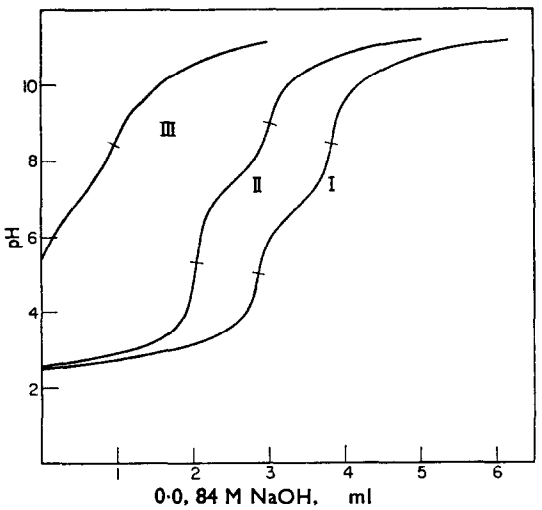

FIG. 1.—pH titration curves, at 25·0 ± 0·1°C.
I—67·3 mg of $H_6XO.2H_2O$; II—52·8 mg of $H_4XO.H_2O$; III—71·7 mg of Dotite XO; each in 50 ml of 0·1*M* KNO_3.

(*i.e.*, for an untitrated solution), which showed the existence of H_3XO^{3-}, H_4XO^{2-}, and H_5XO^-. From equations (4) and (5), $\log k_4 = 2{\cdot}85 \pm 0{\cdot}06$ and $\log k_5 = 2{\cdot}32 \pm 0{\cdot}15$ were calculated. Over the titration range 3–5 ml the solution will contain HXO^{5-}, H_2XO^{4-}, and H_3XO^{3-}. The equilibria correspond to those of H_2I and at 4·30 ml titration $\bar{n} = 0{\cdot}606$, which shows the existence of HXO^{5-}. For the equilibria, $\log k_2 = 10{\cdot}39 \pm 0{\cdot}05$ and $\log k_3 = 6{\cdot}67 \pm 0{\cdot}03$ were calculated.

The calculation of the acid formation constants of SXO is virtually identical with that of XO. $\log k_1 = 10{\cdot}90 \pm 0{\cdot}15$, $\log k_2 = 7{\cdot}44 \pm 0{\cdot}03$, and $\log k_3 = 2{\cdot}60 \pm 0{\cdot}06$ were calculated for the equilibria between SXO^{4-}, $HSXO^{3-}$, H_2SXO^{2-}, and H_3SXO^-. In this report all the constants are mixed constants and the accuracy of each was estimated by considering the accuracy of the pH titration and the absorption measurements.

Calculation of acid formation constants from absorption spectra

Both XO and SXO have a variation in colour over a wide pH range. The concentration of each species is determined from its absorbance. Between pH 2 and 5, however, XO or SXO have identical absorption curves, so the pH method is used for this region. When the equilibria shown in equations (1), (2) and (3) are in existence,

the absorbances should be in accordance with the equation (6).

$$A = \sum_{n=0}^{N} \varepsilon_{H_nI}[H_nI^{(N-n)-}] \tag{6}$$

From equations (2), (3) and (6) we obtain

$$A - C_s\varepsilon_I = \sum_{n=1}^{N} J_n' k_1 k_2 \ldots . k_N \tag{7}$$

$$J_n' = (C_s\varepsilon_{H_nI} - A)[H^+]^n \tag{8}$$

A = Absorbance

ε = Molar absorptivity

J_n' = A parameter used to calculate the acid formation constant.

Acid formation constants are calculated from equations (4), (7) and (8) used as simultaneous equations. The calculation does not necessitate knowledge of C_s and $[H_nI^{(N-n)-}]$, but A, $[H^+]$, and $C_s\varepsilon_{H_nI}$ will suffice so long as C_s is constant. If $C_s\varepsilon_{H_nI}$ cannot be measured, the constants containing it are calculated for many values of A and $[H^+]$, and $C_s\varepsilon_{H_nI}$ and the acid formation constants are derived from them by iterative calculation.

The absorption spectra of $1{\cdot}001 \times 10^{-5}M$ SXO and $8{\cdot}05 \times 10^{-6}M$ XO below pH 2 are shown in Figs. 2, 3 and 4. Figure 4 also shows the curves calculated from the constants determined in the course of this work. Acidity below pH 1 is indicated by the Hammett function H_0.[26,27] From pH 2 to H_0 0·35 the absorption of SXO gradually increases at 510 mμ and below H_0 0·35 SXO has strong absorption at 510 mμ and an isosbestic point at 470 mμ. The equilibria may be among H_4SXO, H_5SXO^+, and H_6SXO^{2+}. From the equations above, $\varepsilon_{H_5SXO} = 1{\cdot}54 \times 10^4$, $\log k_5 = 0{\cdot}53 \pm 0{\cdot}03$, and $\log k_6 = -0{\cdot}65 \pm 0{\cdot}05$ were calculated, using $C_s\varepsilon_{H_4SXO} = 0{\cdot}050$, $C_s\varepsilon_{H_6SXO} = 0{\cdot}670$, and $A = 0{\cdot}105$ (H_0 0·67), 0·201 (H_0 0·045), and 0·565 (H_0 −1·24) at 510 mμ. On the other hand the absorption spectra of XO show three equilibria below H_0 0·5. The absorbance increases at 450–490 mμ in regard to the first equilibrium and at 515 mμ in regard to the second equilibrium near H_0 −1. At 480 mμ, $\varepsilon_{H_7XO} = 1{\cdot}78 \times 10^4$, $\log k_7 = -1{\cdot}04 \pm 0{\cdot}05$, and $\log k_8 = -2{\cdot}29 \pm 0{\cdot}08$ were calculated for the equilibria between H_6XO, H_7XO^+, and H_8XO^{2+}. The absorbances between H_0 −0·86 and −5 were corrected by means of k_7 and k_8. By using the corrected values, $\varepsilon_{H_8XO} = 6{\cdot}45 \times 10^4$, $\log k_6 = -1{\cdot}83 \pm 0{\cdot}06$, and $\log k_9 = -3{\cdot}32 \pm 0{\cdot}08$ were obtained for the equilibria of H_7XO^+, H_8XO^{2+}, and H_9XO^{3+}.

The absorption spectra of SXO between pH 3·7 and 14 are shown in Fig. 5. Near pH 7, $\varepsilon_{HSXO} = 5{\cdot}58 \times 10^4$ and $\log k_2 = 7{\cdot}47 \pm 0{\cdot}03$ were obtained from the pH value corresponding to the mid-point of the absorbance increase at 573 mμ as the pH was raised. Above pH 9 the absorption increases gradually with the addition of alkali, and $\log k_1 = 10{\cdot}90 \pm 0{\cdot}15$ was obtained from the pH value of the mid-point of the absorbances corrected for ε_{HSXO} and k_2.

The absorption spectra of XO between pH 1 and 14 shown in Figs. 6 and 7 are similar to those obtained by Řehák and Körbl[28] but the absorbances are about one and a half times as large. The calculations for XO were carried out as described above, and the results are shown in Table I.

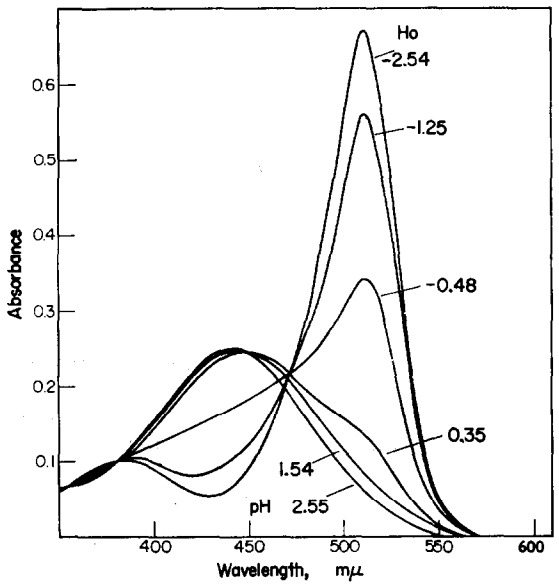

FIG. 2.—Absorption spectra of SXO ($1{\cdot}001 \times 10^{-5}M$ in 1-cm cells, from $H_0 = -2{\cdot}54$ to pH = 2·55).

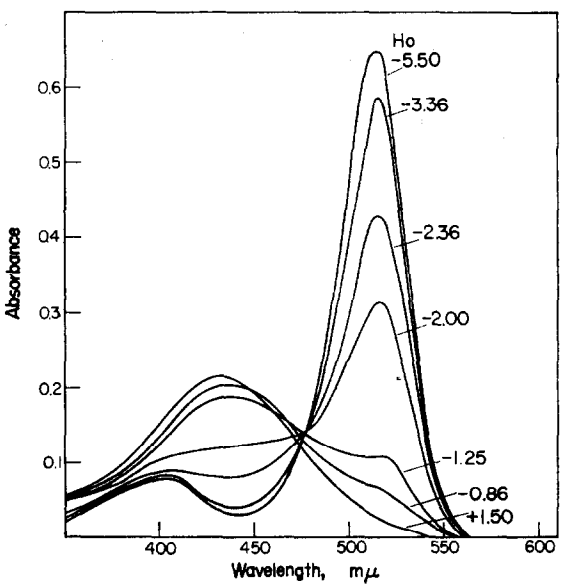

FIG. 3.—Absorption spectra of XO $8{\cdot}05 \times 10^{-6}M$ in 1-cm cells, from $H_0 = -5{\cdot}50$ to $+1{\cdot}50$.

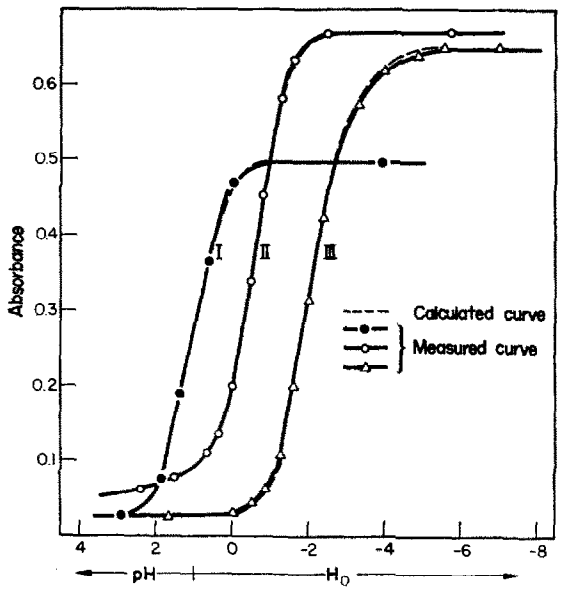

FIG. 4.—Effect of H_0 on absorbance.

I—Cresol Red, $1{\cdot}000 \times 10^{-5}M$ at 520 mμ; II—SXO, $1{\cdot}001 \times 10^{-5}M$ at 510 mμ; III—XO, $8{\cdot}05 \times 10^{-6}M$ at 515 mμ.

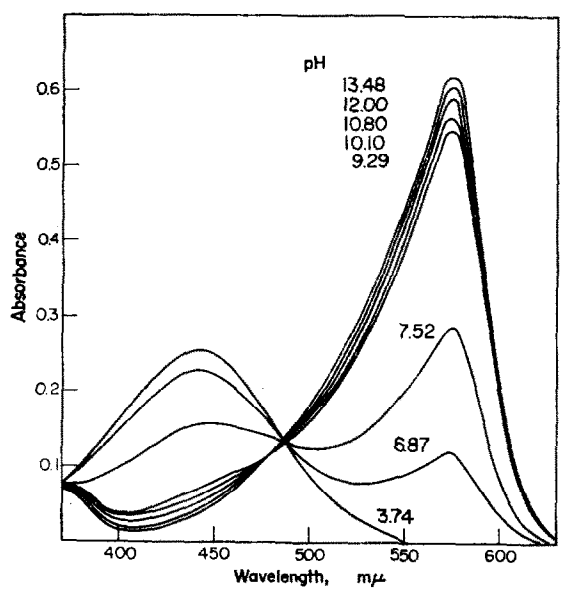

FIG. 5.—Absorption spectra of SXO ($1{\cdot}001 \times 10^{-5}M$ in 1-cm cells, $\mu = 0{\cdot}1$, from pH 3·74 to 13·48).

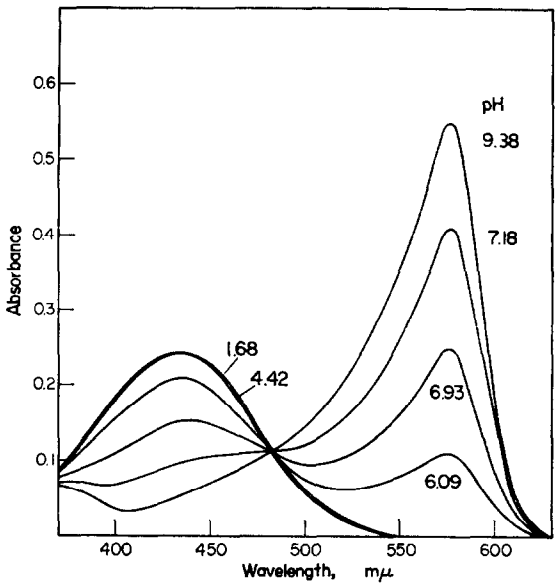

FIG. 6.—Absorption spectra of XO ($9{\cdot}20 \times 10^{-6}M$ in 1-cm cells, $\mu = 0{\cdot}1$, from pH 1·68 to 9·38).

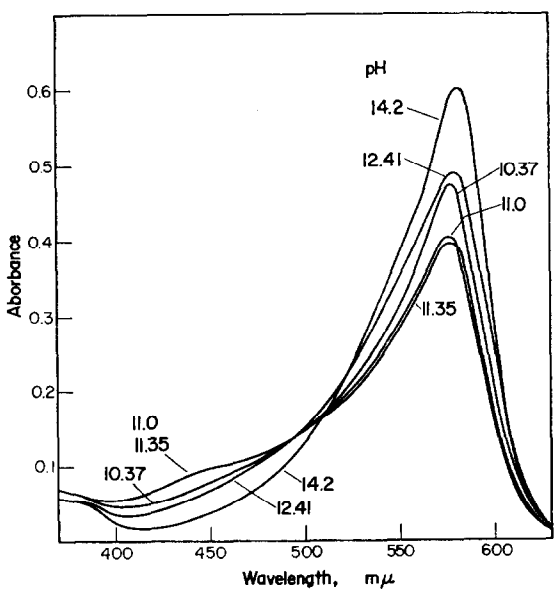

FIG. 7.—Absorption spectra of XO from pH 10·37 to 14·2 (conditions as in Fig. 6).

Effect of ionic strength on the activity of XO

If the equilibrium between red XO and orange XO is that between H_2XO^{2-} and H_3XO^{3-}, the equation will be described[29] by

$$\Delta \log k_3 = \log (\gamma_{H_2XO}/\gamma_{H_3XO})_x - \log (\gamma_{H_2XO}/\gamma_{H_3XO})_o. \quad (9)$$

γ = Activity coefficient of the ion indicated by subscript

$\Delta \log k_3$ = Difference between the apparent and true acid formation constant

Subscripts x and o = Actual and infinitely dilute solution respectively.

When the Debye-Hückel limiting law holds good ($\mu < 0{\cdot}01$), equation (9) becomes

$$\Delta \log k_3 = (3^2 - 4^2) \times 0{\cdot}509 \sqrt{\mu} = -3{\cdot}5 \sqrt{\mu}. \quad (10)$$

The acid formation constants were obtained spectrophotometrically in this way. The results, and data for Cresol Red for comparison,[29] are shown in Fig. 8. The slope is similar to that of equation (10). Cresol Red is a dibasic acid, and gives a slope of $-1{\cdot}5$. This shows that the activity coefficient of XO ion can be calculated from the Debye-Hückel equation, that the equilibrium near pH 7 is between H_2XO^{4-} and H_3XO^{3-}, and that the formation constants of XO-metal chelates are affected by the ionic strength.[30]

The equilibria of SXO

The wavelengths of absorption maxima and the formation constants of XO, SXO, Cresol Red and iminodiacetic acid are shown in Table II. On the alkaline side the equilibrium between the red SXO and yellow SXO corresponds to the dissociation of the hydroxyl group.[31] Above pH 10 the molar absorption of SXO increases gradually, but not that of Cresol Red, so that $\log k_1$ corresponds to $\log k = 9{\cdot}65$ for iminodiacetic acid. Between pH 2 and 5 the colour of the solution has not changed, and $\log k_3$ and $\log k_4$ are similar to those of the carboxyl groups. Below pH 2 the two constants corresponding to those of the quinone and sulphonic acid groups[32] are lower than the constants for Cresol Red ($\log k = 1{\cdot}00$). The constant observed by Olsen and Margerum[3] is compared with $\log k_5$ and $\log k_6$ calculated by us. All the equilibria of SXO are shown in Fig. 9.

The equilibria of XO

The equilibrium constants of XO obtained by Řehák and Körbl[28] are different from ours on the acidic side but similar on the alkaline side. This shows that their sample might have contained about 30% of iminodiacetic acid and a small amount of SXO. The three constants obtained in strongly acidic solution are based on the protonations of the carboxyl, quinone, and sulphonic acid groups, and correspond to the three constants of SXO (k_4, k_5 and k_6).[31,32]

In view of the facts it seems most reasonable to conclude as follows. (1) SXO and XO have one and two di(carboxymethyl)aminomethyl groups respectively. (2) The acid formation constants of SXO and XO are similar to those of Cresol Red and iminodiacetic acid. (3) The protonations of the sulphonic acid and quinone group of

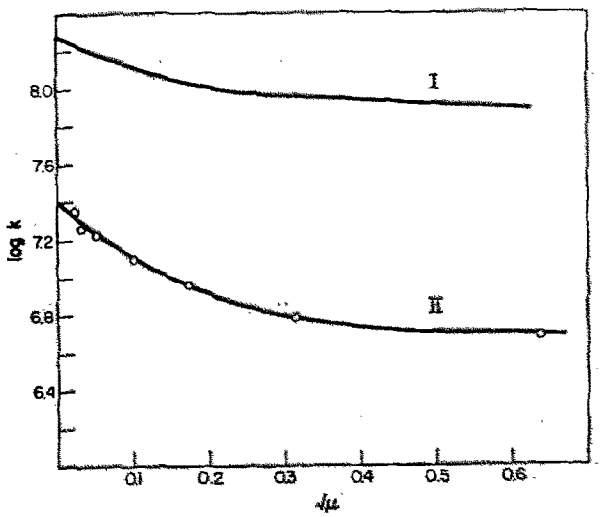

FIG. 8.—Effect of ionic strength on acid formation constants.

Salt used—KNO_3; I—$H^+ + CR^{2-} \rightleftharpoons HCR^-$; II—$H^+ + H_2XO^{4-} \rightleftharpoons H_2XO^{3-}$ (CR = Cresol Red).

SXO and XO are separately observed in strongly acidic medium. (4) The di(carboxymethyl)aminomethyl group is as weakly bathochromic as the methyl group and increases the molar absorptivity; it also influences slightly the non-localized electron of the sulphonphthalein group. As a final check, the curve for *n vs.* pH, calculated from the constants obtained in this work, was compared with the experimentally observed values. The results in Fig. 10 show excellent agreement.

The purity of a commercial XO reagent

From Fig. 1 the molecular weights of XO and SXO were calculated to be 705 ± 5 and 547 ± 3, which agreed well with the theoretical weights of 708·7 for $C_{31}H_{32}O_{13}N_2S.2H_2O$ and 545·5 for $C_{26}H_{25}O_9NS.H_2O$ respectively. The pH titration curve of a commercial XO (Dotite XO) is also shown in Fig. 1. The curve shows the commercial XO to be the trisodium salt with an apparent purity of 109%, but chromatography showed the reagent contained SXO. The absorption curves of pure XO, pure SXO, and the Dotite reagent are shown in Fig. 11. From the absorbances A_{435} at 435 mμ (pH 3·11) and A_{510} at 510 mμ (1·44*M* H_2SO_4) the purity of a sample of XO reagent can be calculated by means of the equations

$$A_{435} = 2{\cdot}62 \times 10^4 C_{XO} + 2{\cdot}52 \times 10^4 C_{SXO} \quad (11)$$

$$A_{510} = 0{\cdot}472 \times 10^4 C_{XO} + 3{\cdot}21 \times 10^4 C_{SXO} \quad (12)$$

where C_{XO} and C_{SXO} = concentrations of XO and SXO respectively, in the reagent solution. From the equations, 36·3% of XO and 17·2% of SXO were found for this trisodium salt. From the reports dealing with the XO–metal chelates, 30–40% of XO and 10–15% of SXO[19,33,34] or 40–50% total of XO and SXO[4,5,12–18,20–23] in the reagents used were calculated from the data of the absorption spectra. The molecular weight of SXO was measured by Olson and Margerum,[3] but the molar absorptivity

TABLE II.—ACID FORMATION CONSTANTS, WAVELENGTHS OF ABSORPTION MAXIMA AND MOLAR ABSORPTIVITIES OF XO, SXO, CRESOL RED, AND IMINODIACETIC ACID

Xylenol Orange				Semi-Xylenol Orange				Cresol Red				Iminodiacetic acid	
Ion	Wavelength	Absorptivity	Equilibrium constant	Ion	Wavelength	Absorptivity	Equilibrium constant	Ion	Wavelength	Absorptivity	Equilibrium constant	Ion	Equilibrium constant
	λ_{max} $m\mu$	$\varepsilon \times 10^{-4}$	$\log k$		λ_{max} $m\mu$	$\varepsilon \times 10^{-4}$	$\log k$		λ_{max} $m\mu$	$\varepsilon \times 10^{-4}$	$\log k$		$\log k$
H_9XO^{3+}	515	8·08 ± 0.06	−3.32 ± 0.08	H_6SXO^{2+}	510	6·69 ± 0.05	−0.65 ± 0.05	H_3CR^+	520	5.00 ± 0.05			
H_8XO^{2+}	515	6·54 ± 0.15	−1.83 ± 0.06	H_5SXO^+	510 †	1·54 ± 0·03†		H_2CR					
H_7XO^+	480†	1·78 ± 0·04†	−1.04 ± 0.05				0·53 ± 0·05						
H_6XO			<1·5*	H_4SXO			<1·5*				1·00 ± 0·05	H_3IDA^+	
H_5XO^-	439 ~	2·62 ± 0·03	2·32 ± 0.15*	H_3SXO^-	443 ~	2·54 ± 0·03						H_2IDA	
H_4XO^{2-}	434		2·85 ± 0.06*		437		2.60 ± 0·06*						2·75 ± 0.08*
H_3XO^{3-}			6·74 ± 0·04	H_2SXO^{2-}			7·47 ± 0·03	HCR^-	435	1·80 ± 0·03		$HIDA^-$	
H_2XO^{4-}	578	6·09 ± 0·04	6·67 ± 0.03* 10·56 ± 0·09	$HSXO^{3-}$	573	5·58 ± 0·03	7·44 ± 0·03*	CR^{2-}	572	4·97 ± 0·04	7·95 ± 0·03		
HXO^{5-}	578	3·66 ± 0·25	10·39 ± 0.05*				10·90 ± 0·15						9·65 ± 0.05*
			12·23 ± 0·05				10·90 ± 0·15*						
XO^{6-}	582	6·54 ± 0·05		SXO^{4-}	576	6·20 ± 0·03						IDA^{2-}	

* Data measured by means of pH titration; the rest by means of spectrometry.
† Data obtained near absorption maximum.

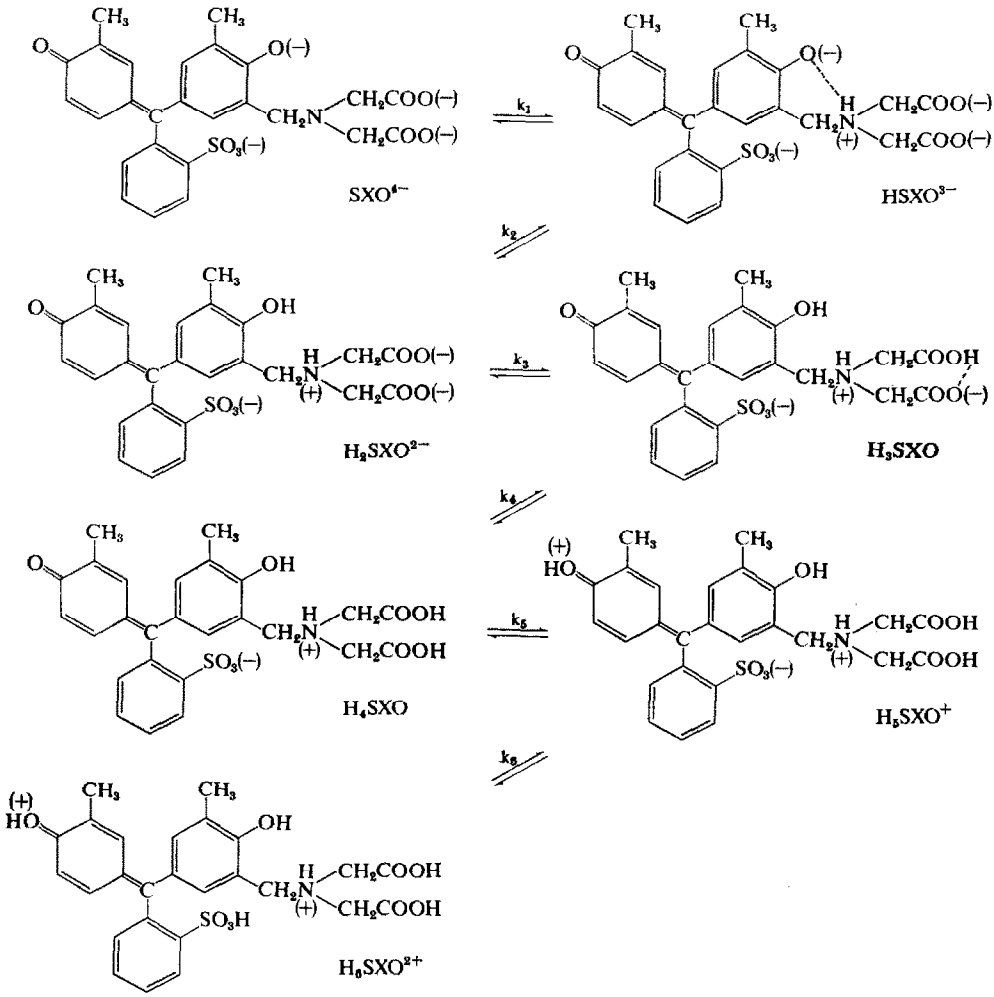

FIG. 9.—Equilibria of SXO.

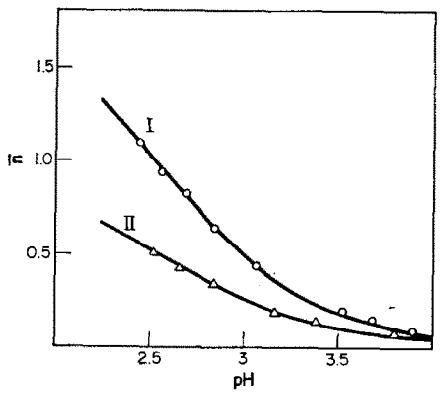

FIG. 10.—Plots of $\bar{n}_{exp}$ and curve of $\bar{n}_{calc}$ against pH.
I—XO, shown as $H_3(H_3XO)$; II—SXO, shown as $H_2(H_2SXO)$.

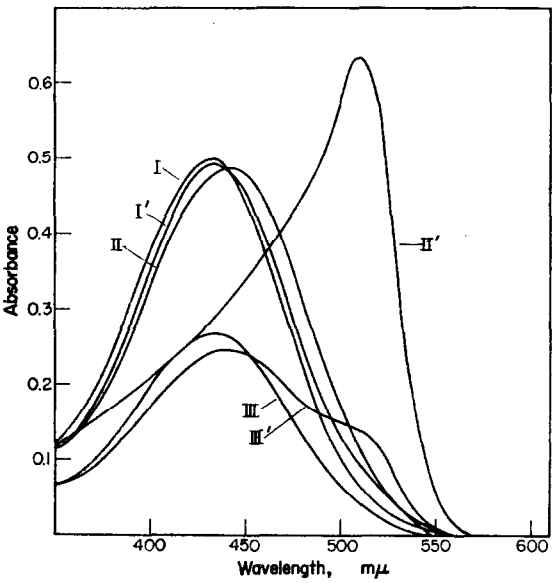

FIG. 11.—Absorption spectra of pure XO, pure SXO and Dotite XO.
At pH 3·11, $\mu = 0{\cdot}1$; I—XO; II—SXO; III—Dotite XO.
In 1·44M H_2SO_4; I'—XO; II'—SXO; III'—Dotite XO.
(XO—1·908 × $10^{-5}M$, SXO—1·928 × $10^{-5}M$, Dotite XO—2·00 × $10^{-5}M$).

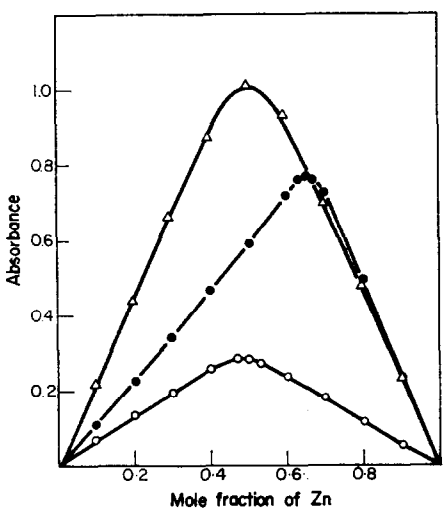

FIG. 12.—Job's curves for zinc complexes.
●—Zn-XO, [Zn] + [XO] = 3·86 × $10^{-5}M$, $\mu = 0{\cdot}1$, pH 6·21, 1-cm cells at 573 mμ;
○—Zn-SXO, [Zn] + [SXO] = 3·88 × $10^{-5}M$, $\mu = 0{\cdot}1$, pH 6·30, 1-cm cels, at 500 mμ;
△—Zn-impure XO,[20] [Zn] + [XO] = 5 × $10^{-4}M$, $\mu = 0{\cdot}04$, pH 6·0, 1-cm cell, at 574 mμ.

used was only 66% of that found by us. Impure XO and SXO may contain 30–50% of iminodiacetic acid which is difficult to remove by means of recrystallization. Figure 12 shows that XO and SXO form 1:2 and 1:1 chelates respectively with Zn(II) (*i.e.*, $XOZn_2$ and SXOZn), but Šťudlar and Janoušek's curve[20] shows a 1:1 chelate.

Although many papers have claimed that Methylthymol Blue[35–38] and XO[7,10,14–20,23,30,34,39–41] form 1:1 chelates with many metals, it now seems that XO forms at least some 1:2 chelates.

Résumé—On a chromatographié un mélange de Xylénol Orangé (XO) et de Semi-Xylénol Orangé (SXO) sur une colonne de cellulose puis procédé à l'échange d'ions avec la résine Diaion SK-1. On a titré XO et SXO sous formes acides par la soude pour déterminer les basicités et les constantes de formation d'acide. On a mesuré les spectres d'absorption de XO et SXO dans un large domaine de pH et les a utilisés pour le calcul des constantes de formation d'acide, des absorptions moléculaires et de l'effet de la force ionique sur l'activité de XO. On a mesuré la pureté d'un XO commercial par spectroscopie d'absorption et a trouvé que l'échantillon contenait 36,3% de XO et 17,2% de SXO. XO et SXO purs forment des complexes 1:2 et 1:1 respectivement avec Zn (II). Sur la base de ces données, on a comparé la structure ionique de XO et SXO à celles du Rouge de Crésol et de l'acide iminodiacétique et en discute.

Zusammenfassung—Ein Gemisch von Xylenolorange (XO) und Semi-Xylenolorange (SXO) wurde an einer Cellulosesäule chromatographiert und mit Diaion SK-1 dem Ionenaustausch unterworfen. XO und SXO wurden in saurer Form mit Natriumhydroxid titriert, um Basizitäten und Dissoziationskonstanten zu bestimmen. Die Absorptionsspektren von XO und SXO wurden in einem großen pH-Bereich gemessen und zur Berechnung der Dissoziationskonstanten, der molaren Extinktionskoeffizienten und des Einflusses der Ionenstärke auf die Aktivität von XO herangezogen. Die Reinheit von käuflichem XO wurde durch Absorptionsspektrometrie geprüft; die Probe enthielt 36,3% XO und 17,2% SXO. Reines XO und SXO bilden einen 1:2- bzw. 1:1- Komplex mit Zink(II). Auf Grund dieser Daten wurde die Ionenstruktur von XO und SXO mit der von Kresolrot und Iminodiessigsäure verglichen und diskutiert.

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DIRECT TITRATION OF GLYCEROL BY CONSTANT CURRENT POTENTIOMETRY

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Summary—A direct, constant-current potentiometric titration method allows quantitative determination of 0·50–5·00 mg samples of glycerol in aqueous solution with errors ranging from 0·2% for the large samples to 2·0% for the smaller samples. Perchloratocerate is used as the standard oxidant and pyrolytic graphite as the electrode material. A direct determination is made possible by elevated temperatures, high acidity, and a relatively large constant current. Sources of error and possible interferences are discussed.

BECAUSE of its wide use and natural occurrence many methods have been devised for the determination of glycerol in aqueous solution. The convenience and simplicity of the "wet" volumetric methods account for their continued importance. The most common of these are esterification to the triacetate followed by hydrolysis and an acid–base titration, and oxidation by excess of chromate, periodate or cerate followed by back-titration of the excess oxidant. The indirect cerate titration was first described by Smith and Duke,[6] who showed that the reaction rate in perchloric acid was definitely higher than in sulphuric acid solution. The equation indicating the stoichiometry is as follows:

$$8Ce^{4+} + C_3H_5(OH)_3 + 3H_2O \rightarrow 3HCOOH + 8Ce^{3+} + 8H^+$$

The work presented here describes the direct titration of glycerol in perchloric acid solution by constant-current potentiometry[4] with pyrolytic graphite electrodes (PGE). Miller and Zittel[2] have shown the apparent reversibility of the cerate–cerous system at a pyrolytic graphite cathode.

EXPERIMENTAL

The electrodes used were two $\frac{1}{4} \times \frac{1}{4} \times \frac{1}{4}$ in. rods of pyrolytic graphite with the higher conductivity along the rod axis. The sides of the cathode were covered with a mixture of 80% Epolene C-10® (Eastman-Tennessee) and 20% high-melting paraffin wax, leaving only the end of the cathode exposed. The constant current in the system was maintained by a 90-V battery in series with a 900,000 ohm resistor. A commercially available pH meter with 0–1400 mV scale, or a digital vacuum tube voltmeter, was used to measure the potential difference between the two pyrolytic graphite electrodes.

Titrations were carried out in 150-ml beakers. A combination heater–magnetic stirrer was used to heat and stir the titration solutions. A heat reservoir in the form of a water-bath or an aluminium block maintained the temperature sufficiently constant during the titration.

Reagents

All chemicals were reagent grade and used as supplied. The perchloratocerate was prepared by mixing ammonium hexanitratocerate with enough concentrated perchloric acid to give a solution 2*F* in perchloric acid when diluted. Any hydrolysis precipitates were removed before the solution was standardized and used.

Procedure

Two pyrolytic graphite electrodes polarized by a 100-μA constant current, were immersed in a stirred solution of 2*F* perchloric acid which was heated to 80°. The glycerol sample was then added

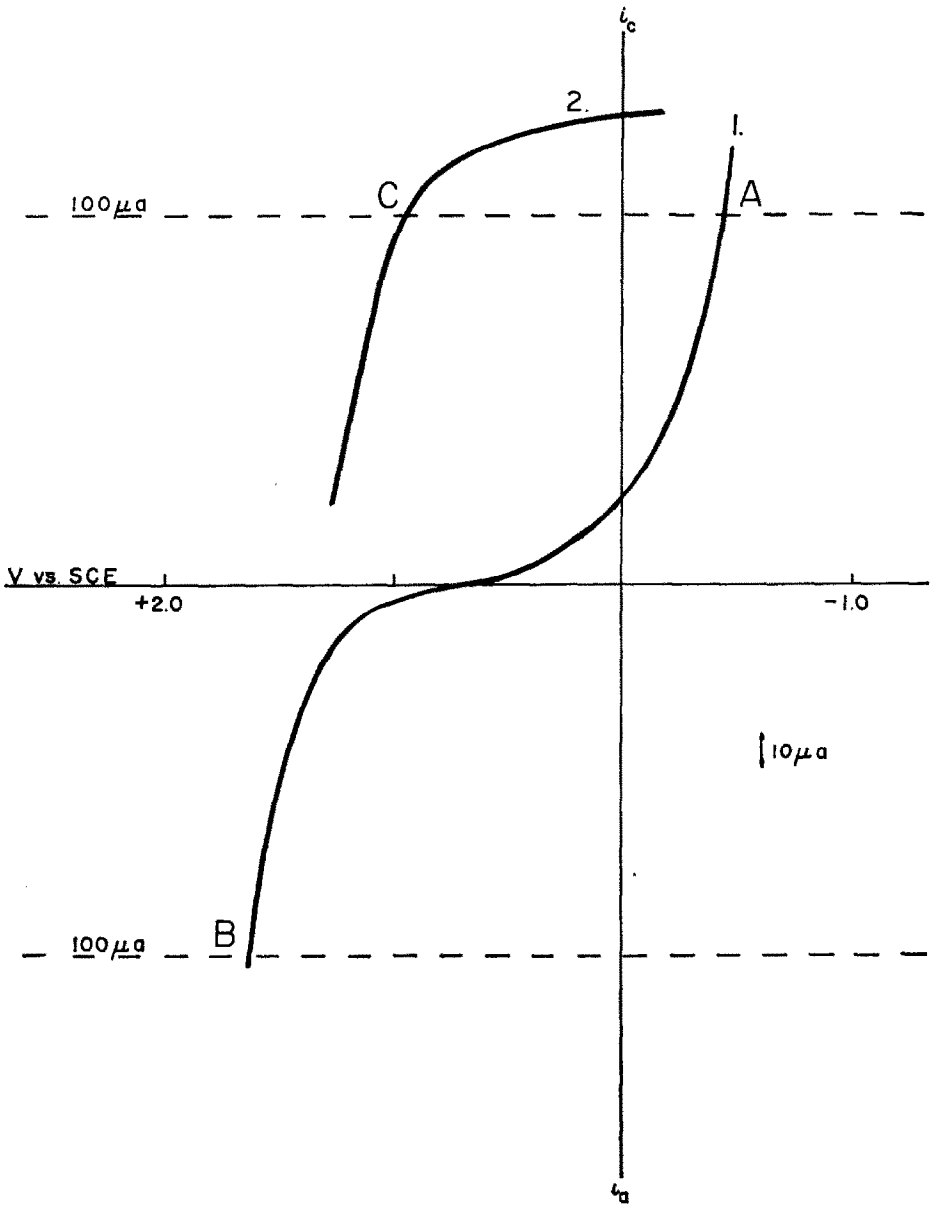

FIG. 1.—Current–voltage curves in 2*F* $HClO_4$ at 25°C.
1. Residual current. 2. Cerate reduction.

to the heated solution. The resulting solution was titrated with the perchloratocerate until the voltage between the electrodes changed to 0·3 V from initially high values of about 1·6 V. The end-point was defined as the volume at which a one-drop increment of titrant caused the potential to remain at or below 0·3 V for 30 sec. A blank was determined.

RESULTS AND DISCUSSION

The accuracy and precision of the proposed method were established by comparing the volume of titrant used for several direct titrations of 5-ml aliquots of 0·01114*M* glycerol solution with the volume used in a well-established indirect cerate oxidation method.[5] The results of this comparison are summarized in Table I. This table

TABLE I

Direct determination of 5·13 mg of glycerol		Indirect determination of 5·13 mg of glycerol	
Found, *mg*	Error, *mg*	Found, *mg*	Error, *mg*
5·12	−0·01	5·28	+0·15
5·12	−0·01	5·14	+0·28
5·05	−0·08	5·32	+0·19
5·20	+0·07	4·88	−0·25
5·19	+0·06	5·12	−0·01
5·17	+0·04	5·04	−0·09
5·10	−0·03	4·89	−0·24
5·15	+0·02	5·19	+0·06
Mean 5·14		Mean 5·14	
Std. devn. 0·05		Std. devn. 0·20	

illustrates the agreement between the indirect and direct methods in the 5·00-mg range. Greater precision was obtained for the direct method. This was presumably a result of the fewer manipulations needed in it.

Observation of the current–voltage curves for the perchloratocerate ion in acid solution at a pyrolytic graphite electrode (Fig. 1) indicates nearly reversible behaviour of the cerate-cerous system in the vicinity of 0·90 V (*vs.* S.C.E.). This is in distinct contrast to the highly irreversible reduction of cerate which occurs at other common electrodes. The titration curve of glycerol (Fig. 2) can be interpreted in terms of the current–voltage curves shown in Fig. 1. The potential at the beginning of the titration is determined by the intersection of the 100-μA constant current lines with current–voltage curve 1. The potential difference is indicated by the two points *A* and *B*. With the exception of a slight increase at the beginning of the titration, the voltage remains constant across the electrodes until an excess of cerate in the solution causes a shift in the cathode reaction from curve 1 to curve 2, and a corresponding potential drop from *AB* to *CB* which indicates the end-point of the titration.

The faster reaction rate needed for a direct determination was obtained by using elevated temperatures, high acid concentration, and a relatively large constant current (100 μA).

At temperatures below 70° the reaction is slow enough to make direct titration impractical. At the recommended temperatures delays due to slow reaction rate are still perceptible, but a titration can easily be performed in less than 10 min.

A 2*F* mineral acid solution was used as the solvent for the titration because the reaction rate is favoured by high acidity.[1] Perchloric acid was selected as the most suitable of the strong mineral acids. Nitric acid can be used, but the reaction is

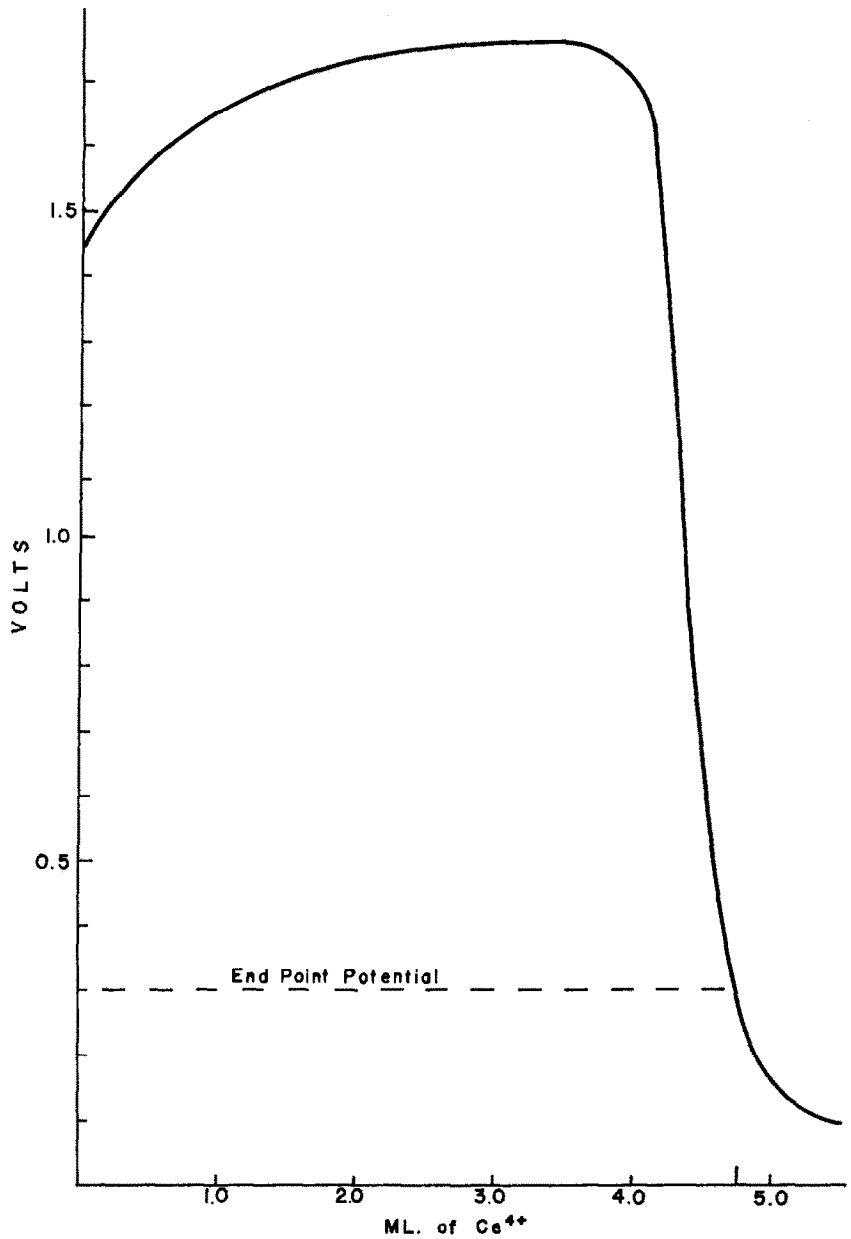

FIG. 2.—Titration curve for glycerol with perchloratocerate.

slightly slower. Guilbault and McCurdy[1] have shown that sulphate and bisulphate ions affect the reaction rate adversely. Chloride is oxidized under these conditions.

Titration at the relatively large constant current of 100 μA provides for a definite excess of titrant at the end-point, and thus a significant decrease in reaction time. Positive error is avoided by use of a blank titration at the same current. Figure 2 indicates also that the voltage change at the end-point is quite large and unmistakable

when this current is used. When a thermostatically controlled combination heater–stirrer is used, current drain by the heater coils may cause fluctuations in the stirring rate. Turning the heater coils off prior to reading the end-point potentials prevents such fluctuations. The stirring rate at the blank end-point and the end-point of the actual glycerol determinations must be the same in order to maintain the accuracy and the precision of the proposed method.

Sample loss due to evaporation was estimated, using Raoult's law. Such computations indicated that less than 0·1 % of a 5-mg sample volatilized during a 10-min titration. As an experimental check, several titrations were carried out in an Erlenmeyer flask fitted with a water-cooled condenser. These titrations showed no significant deviation from those performed in open beakers.

The large shift toward more positive cathode potentials at the end-point was quite definite, but somewhat slow. This is evidence to support the formation of an electrode film as suggested by Miller and Zittel.[3] Slow potential increases at the beginning of the titration were found to be anodic and are presumably due to electrochemical oxidation of the anode, or to film formation at the surface of the anode by temporary local concentrations of cerate. Neither of these effects significantly affects titration accuracy or convenience.

Reference to Fig. 2 indicates that in principle any potential along the relatively large potential shift could be selected for end-point indication. Titrating to 0·3 V allows the major portion of the potential shift to provide a convenient anticipation of the end-point. In addition, this potential is positive relative to the region where film formation occurs,[3] thereby eliminating spurious potentials resulting from alternate formation and reduction of the film.

Several titrations were carried out with more dilute solutions of glycerol and/or cerate to test the sensitivity limits of the method. Table II shows that less than 1 mg

TABLE II.—TITRATION SENSITIVITY

Sample number*	Cerate concentration, *M*	Glycerol present, *mg*	Glycerol found, *mg*	Relative error, %
1	0·09629	5·29	5·30	+0·2
2	0·09629	2·64	2·61	−0·8
3	0·09629	0·53	0·54	+1·9
4	0·04814	5·29	5·27	−0·4
5	0·00963	5·29	5·27†	−0·4
6	0·00963	2·64	2·60†	−1·5
7	0·00963	0·53	0·52†	−1·9

* Each individually listed result is an average of several results.
† These values were corrected for dilution caused by the addition of titrant.

of glycerol could be determined accurately by this method. When dilute perchloratocerate solutions (approx 0·01*M*) were used, corrections were made for the relatively large increases in the volume of titration solution. The negative errors found for the most dilute solutions may be due to anodic reoxidation of cerium(III). Titrations at greater dilutions than those presented here would be inconveniently slow.

Cerate solubility limits the titrant concentration to about 0·1*M*. Thus titration of samples larger than about 5·0 mg is not feasible unless rather large dilution corrections are applied.

Since no electrode which was sensitive to glycerol concentration was known, the major requirement for a suitable anode was that it should keep at constant potential in the vicinity of the end-point. Copper, platinum, gold, pyrolytic graphite, and a saturated calomel electrode were tested as possible anodes. The last was rejected because of the difficulties with the salt bridge at the temperatures used. Pyrolytic graphite was selected as the most suitable of the solid anode materials because it provided the most stable anode potentials under these conditions.

A study was conducted to see what interferences could be tolerated in the determination. As expected, easily oxidized or hydrolysed organic compounds interfere. Such interferences are less severe in the direct method than in the indirect method, because direct titration minimizes the concentrations of excess titrant. Neither saturated acids nor alcohols interfere significantly at concentrations up to $\frac{1}{10}$ that of the glycerol.

Acknowledgement—Mr. Gerald Nelesen obtained the current–voltage plots.

Zusammenfassung—Ein direktes potentiometrisches Titrationsverfahren bei konstanter Stromstärke erlaubt die quantitative Bestimmung von 0,50–5,00 mg-Proben Glycerin in wäßriger Lösung mit Fehlern von 0,2% bei den großen und 2,0% bei den kleineren Probemengen. Perchloratocerat wird als eingestelltes Oxidationsmittel verwandt und pyrolytischer Graphit als Electrodenmaterial. Die direkte Bestimmung wird ermöglicht durch erhöhte Temperatur, hohe Acidität und eine relativ große konstante Stromstärke. Fehlerquellen und mögliche Störungen werden diskutiert.

Résumé—Une méthode directe de titrage par potentiométrie à courant constant permet le dosage quantitatif d'échantillons de glycérol de 0,50 à 5,00 mg en solution aqueuse avec des erreurs comprises entre 0,2% pour les gros échantillons et 2,0% pour les échantillons les plus petits. On utilise le perchloratocérate comme oxydant standard et le graphite pyrolytique comme matière d'électrode. Une détermination directe est rendue possible aux températures élevées, forte acidité et courant constant relativement fort. On discute des sources d'erreur et des interférences possibles.

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ELEKTRONISCHES RECHNEN IN DER ANALYTISCHEN CHEMIE—III*

ALGOL-PROZEDUREN ZUR KORRELATIONSRECHNUNG

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Zusammenfassung—An gleichartigen Objekten oder Vorgängen gemessene variable Merkmalsgrößen können nach zunächst unbekannten Gesetzen miteinander verknüpft sein. Realität und Straffheit des Zusammenhanges der Datenreihen im Rahmen vorgegebener Korrelationsfunktionen sind durch die mathematisch-statistische Auswertemethode der Korrelationsrechnung überprüfbar. Im folgenden werden die mathematische Struktur der erforderlichen Rechenprozesse beschrieben und in der problemorientierten Sprache ALGOL als universell verwendbare Prozeduren (Unterprogramme) KORR und TEST formuliert. Es wird gezeigt, daß derartige Universal-Prozeduren SCHWARZE KÄSTEN im Sinne der kybernetischen Terminologie darstellen, die als Bausteine ohne Kenntnis des mathematischen Inhaltes verwendet werden können. Das Schreiben eines Rahmenprogrammes für spezielle Problemstellungen wird dadurch so wesentlich vereinfacht, daß dies nach kurzer Schulung auch ohne mathematische Vorbildung einwandfrei durchgeführt werden kann. An einem praktischen Beispiel wird demonstriert, wie insgesamt 6 Korrelationsansätze und 9 Vergleiche von Korrelationskoeffizienten programmiert und in 9 min elektronisch ausgewertet werden. Der Zeitbedarf bei konventioneller Rechentechnik ist mehr als 100-fach größer.

WESENTLICHE VERWENDETE BEGRIFFE UND SYMBOLE (ALGOL-SYMBOLE IN KLAMMERN)

Gesamtanzahl parallel ermittelter Meßdaten	n	(N)
Laufzahl für Einzelgrößen	i	(I)
Formaler Hauptparameter der Regressionsgeraden	y	(Y)
Formaler Nebenparameter der Regressionsgeraden	x	(X)
Konstantes Glied der Regressionsgeraden (formal)	$[U]$	(U)
Steigung der Regressionsgeraden (formal)	$[V]$	(V)
Korrelationskoeffizient	r_{xy}	(R)
Bestimmtheitsmaß	$r_{xy}^2 = B$	(B)
Prüfgröße für Realität und Straffheit	τ_r	(TAU)
Standardabweichung in Y-Einheiten	$[s_K]$	(SK)
Mittlerer Fehler von $[U]$	$[s_U]$	(SU)
Mittlerer Fehler von $[V]$	$[s_V]$	(SV)
t-Werte der t-Verteilung (t_1, t_2, t_3)	t	(T.)
Boole'sche Variable ($V1$, $V2$, $V3$)	V	(V.)
Prüfgröße zum Vergleich von Korrelationskoeffizienten	λ_r	(L)

Weitere Größen sind im Text eindeutig definiert.

* Teil I—*Talanta*, 1967 **14**, 361, Teil II—*Talanta*, 1967.

EINFÜHRUNG

Problemstellung

Liegen für n gleichartige Objekte oder Vorgänge chemische, physikalische oder sonstige variable Merkmalsgrößen vor, so bildet der eindeutige Nachweis eines Zusammenhanges—einer KORRELATION—zwischen den einzelnen Merkmalen oft die Basis wertvoller neuer Erkenntnisse. Im einfachsten Falle wird eine Korrelation zwischem einem

Hauptmerkmal mit n Merkmalsgrößen y_1

und einem

Nebenmerkmal mit n Merkmalsgrößen x_1

hinsichtlich Realtität und Straffheit zu beurteilen sein, wobei eine geeignet erscheinende Korrelationsfunktion $y = F(x)$ vorzugeben ist. Bei mehreren Nebenmerkmalen $x(1)_1, x(2)_1, \ldots, x(J)_1, \ldots$ resultiert als Korrelationsfunktion:

$$y = F\{x(1), x(2), \ldots, x(J), \ldots\} \tag{1}$$

Die einfachste Form der korrelativen Datenauswertung ist die EINFACHE LINEARE KORRELATIONSRECHNUNG bei der die Größen des Hauptmerkmals und des Nebenmerkmals bzw. der Nebenmerkmale zunächst durch Substitution so umgeformt werden müssen, daß eine Linearfunktion (REGRESSIONSGERADE)

$$Y = [U] + [V] \cdot X \tag{2}$$

erhalten wird. Sowohl für die „formalen Parameter" Y als auch für X können beliebige Funktionen der „aktuellen Parameter" y, x oder y, $x(1)$, $x(2), \ldots, x(J), \ldots$ eingesetzt werden, wie z.B.

$$\text{für } Y\text{: } \ln y \text{ oder } \sin y \text{ oder } y^2 \text{ oder } y/x \text{ oder } y \cdot \sqrt{x}$$

$$\text{für } X\text{: } e^{-x} \text{ oder } \ln(1 + x^3) \text{ oder } x(1) - x(2) \text{ oder } \cos\left\{\frac{x(3)}{x(1)}\right\}.$$

Weitere Beispiele siehe Gottschalk.[1] Bei mehreren Merkmalen besteht prinzipiell die Möglichkeit, die Auswertung des Datenmaterials durch eine MEHRFACHE LINEARE KORRELATIONSRECHNUNG zu erweitern und zu verfeinern. Hierauf wird in dieser Arbeit nicht eingegangen.

Das Ziel einer Korrelationsrechnung ist zunächst die Ermittlung der Korrelationsgrößen

r_{xy} = Korrelationskoeffizient

B = Bestimmtheitsmaß

τ_r = Prüfgröße für Realität und Straffheit der Korrelation

Danach ist τ_r mit den Integralgrenzen t_1, t_2, t_3 der t-Verteilung zu vergleichen.

Wird keine Korrelation ($\tau_r < t_1$) gefunden, so entfallen weitere Rechnungen. Bei zumindest wahrscheinlicher Korrelation ($\tau_r \geqq t_1$) sind in einer weiteren Auswertungsstufe die Regressionsgrößen

$[U]$, $[V]$ = Konstanten der Regressionsgeraden

$[s_K]$ = Standardabweichung in Y-Einheiten

$[s_U]$, $[s_V]$ = „mittlerer" Fehler von $[U]$ bzw. $[V]$

zu berechnen.

Unterschiede in den Korrelationskoeffizienten für Funktionen, die gleichartige Objekte oder Vorgänge mathematisch beschreiben sollen, können über den λ-TEST beurteilt werden.

Es muß hier ausdrücklich darauf hingewiesen werden, daß der formal gesicherte Nachweis einer Korrelation keinesfalls besagt, daß der durch die vorgegebene Korrelationsfunktion beschriebene Zusammenhang von Größen in jedem Falle sinnvoll ist. Eine sinnlose Ausgangs-Fragestellung—etwa nach dem Zusammenhang zwischen dem stündlichen Wasserverbrauch und der Zahl der stündlich eingehenden Analysenproben in einem Laboratorium—erhält nicht dadurch einen Sinn, daß vielleicht formal mathematisch ein Zusammenhang nachweisbar ist. Bevor man eine oder mehrere Korrelationsfunktionen aufstellt und rechnerisch verarbeitet, muß sehr sorgfältig geprüft werden, ob eine logische Verknüpfung überhaupt vorhanden oder zumindest denkbar ist. Bei zeit- oder mengensynchronen Meßdaten an EINEM Objekt oder Vorgang kann dies jedoch fast immer vorausgesetzt werden. Ein anderes Problem stellt die Auffindung einer optimalen Korrelationsfunktion dar. Unter einer Reihe rechnerisch verarbeiteter Funktionsansätze zeichnet sich die Optimalfunktion dadurch aus, daß sie MÖGLICHST EINFACH ist und unter ähnlichen Ansätzen den höchsten Korrelationskoeffizienten r_{xy} und damit auch die kleinste Standardabweichung $[s_K]$ besitzt. Die Verbal-Aussage „einfach" bedeutet eine Dateninterpretation durch Funktionen mit einer kleinen Anzahl k an Funktionskonstanten, d.h. einem großen Freiheitsgrad $f = n - k$. Darüber hinaus ist der wissenschaftliche Erkenntniswert eines Ansatzes häufig erst dann ausreichend belegt, wenn er aus bekannten, chemischen, physikalischen oder sonstigen Gesetzen synthetisch aufgebaut oder abgeleitet werden kann.

Die Durchführung von Korrelationsrechnungen für eine Vielzahl denktheoretisch möglicher Funktionen ist bei Anwendung konventioneller Rechenmethoden eine zeitraubende und fehleranfällige Routinearbeit, die mit Recht gescheut wird, da sie das schöpferisch wissenschaftliche Arbeiten für Tage oder sogar Wochen blockiert. Im folgenden wird gezeigt, daß es neuartige Programmier- und Rechentechniken im Rahmen der elektronischen Informationsverarbeitung gibt, die in wenigen Minuten zu zuverlässigen Resultaten und Urteilen führen.

Elektronische Datenverarbeitung

Wie in den Arbeiten I (Modellanalysen)[2] und II (Varianzanalyse)[3] werden nachfolgend die Programme in der problemorientierten Sprache ALGOL (ALGO-rithmic L-anguage) unter Verwendung der für das Codesystem ALCOR CCIT zulässigen Zeichen formuliert.

Die formalen Parameter Y und X der Korrelationsfunktion (2) können, wie bereits ausgeführt wurde, beliebige arithmetische Ausdrücke aus parallel ermittelten Merkmalsgrößen beinhalten. Bei n Datengruppen ist eine n-fache gleichartige Überführung der ermittelten Meßdaten in Y- bzw. X-Größen erforderlich, was bei 5 verschiedenen Ansätzen von Korrelationsfunktionen immerhin die Durchführung von $5.n$ Rechenoperationen von oft komplizierter Natur bedeutet. Es wäre bei diesem Tatbestand umständlich und zeitraubend, wenn für jeden Korrelationsansatz ein spezielles Programm erstellt, erprobt und gerechnet werden müßte. Hier bietet ALGOL mit den als PROZEDUR bezeichneten Unterprogrammen einen Ausweg. Eine Prozedur braucht nur einmalig mit FORMALEN PARAMETERN formuliert und

kann sodann nach Vereinbarung in einem RAHMENPROGRAMM beliebig oft unter Ersatz der formalen durch AKTUELLE PARAMETER aufgerufen werden. Bei jedem Aufruf wird das formale mathematische Modell der Prozedur aktuell durchgerechnet.

Die nachfolgend aufgeführte Prozedur TEST zum Vergleich von Korrelationskoeffizienten ist sehr einfach aufgebaut. Die entsprechende Vereinbarung beginnt mit

'PROCEDURE' TEST (N1, N2, R1, R2); ....

Nach dem Vereinbarungs-Wortsymbol 'PROCEDURE' folgt der gewählte Prozedurname TEST und danach die in runde Klammern eingeschlossene Liste der formalen Parameter, die aus den Datenumfängen $n_1 =$ N1 und $n_2 =$ N2 sowie aus den zugehörigen Korrelationskoeffizienten $r_{xy}(1) =$ R1 und $r_{xy}(2) =$ R2 der zu vergleichenden Korrelationsansätze besteht. Der weitere Inhalt der Prozedur an Vereinbarungen und Anweisungen braucht hier nicht diskutiert zu werden. Sind nun in einem Rahmenprogramm 3 Korrelationsrechnungen mit Resultaten

$r_{11} =$ R11 aus $n_{11} =$ N11 Daten
$r_{12} =$ R12 aus $n_{12} =$ N12 Daten
$r_{13} =$ R13 aus $n_{13} =$ N13 Daten

erhalten worden, so genügen zur Durchführung der $\binom{3}{2} = 3$ möglichen Vergleiche r_{11} mit r_{12}, r_{11} mit r_{13}, r_{12} mit r_{13} lediglich die Aufrufe:

TEST (N11, N12, R11, R12);
TEST (N11, N13, R11, R13);
TEST (N12, N13, R12, R13);

im Anweisungsteil des Rahmenprogrammes.

Es liegt nahe, auch die Korrelationsrechnung selbst als Prozedur zu formulieren, etwa mit den formalen Eingangsparametern $n =$ N,X,Y,$t_1 =$ T1, $t_2 =$ T2 und $t_3 =$ T3 und dem für Vergleiche benötigten formalen Ausgangsparameter $r_{xy} =$ R. In einer gewöhnlichen Prozedur wären X und Y als Felder zu vereinbaren, da sie stellvertretend für jeweils n Größen mit der Laufzahl $i =$ I $= 1$ bis n stehen. Durch eine von dem dänischem Mathematiker Jensen endeckte und an einfachen Beispielen[4] beschriebene Variante der ALGOL-Prozedur wird es jedoch möglich, X und Y als gewöhnliche Variable einzuführen, wenn zusätzlich die Laufzahl $i =$ I als formaler Parameter aufgelistet wird. Die Vereinbarung einer Jensen-Prozedur beginnt mit

'PROCEDURE' KORR (N, I, Y, X, T1, T2, T3, R); ....

Im Gegensatz zur gewöhnlichen Prozedur mit X- und Y-Feldern, dürfen in der Jensen-Prozedur die X- und Y-Variablen in Aufrufen durch arithmetische Ausdrücke ersetzt werden, die mit aktuellen Feldgrößen formuliert sind. Damit können beliebige Korrelationsansätze unmittelbar in Prozeduraufruf realisiert und spezielle Substitutionsrechnungen im Rahmenprogramm erspart werden. Mögliche Zusammenhänge z.B. zwischen einer Konzentration C und Meßgröße W mit Ansätzen

$$C = [A1] + [B1] \,.\, W^2$$
$$C = [A2] \,.\, W + [B2] \,.\, W^2 \quad \text{umgeformt zu} \quad \frac{C}{W} = [A2] + [B2] \,.\, W$$
$$C = [A3] + [B3] \,.\, \exp\left(\tfrac{1}{2}W\right)$$

lassen sich mit den aktuellen Feldgrößen C[I] und W[I] im Rahmenprogramm direkt als Rechenanweisungen

KORR (N, I, C[I], W[I] × W[I], T1, T2, T3, T4, R1);

KORR (N, I, C[I]/W[I], W[I], T1, T2, T3, T4, R2);

KORR (N, I, C[I], EXP (W[I]/2), T1, T2, T3, T4, R3);

aufrufen.

Im Sinne der kybernetischen Terminologie stellen die Prozeduren SCHWARZE KÄSTEN (black boxes) dar. Es sind dies in sich geschlossene universelle Bausteine, die innerhalb eines Rahmensprogrammes beliebig oft verwendet werden können und zwar auch von solchen Mitarbeitern, die den im Inneren des Schwarzen Kastens konservierten mathematischen Mechanismus gar nicht verstehen oder bereits wieder vergessen haben. Mit wenigen genau festgelegten aktuellen EINGANGS-Informationen werden automatisch ganz bestimmte vorher bekannte aktuelle AUSGANGS-Informationen erhalten. Dieser reine INPUT/OUTPUT-Prozeß unterscheidet sich grundsätzlich nicht von der selbstverständlichen Bedienung zahlreicher schwarzer Kästen, die die technische Entwicklung uns zur Verfügung gestellt hat. Auch bei Gebrauch etwa eines Radioapparates wird ein Input in Form des Einschaltens, der Senderwahl sowie der Lautstärke- und Tonhöheneinstellung nach einem uns zumeist unbekannten Mechanismus in ein Output von Tönen oder Sprachsendungen umgesetzt, wobei der Benutzer es als höchst überflüssig erachtet, vorher das komplizierte Schaltschema und die physikalischen Grundlagen des Sende- und Empfangprozesses verstehen zu wollen.

Die außerordentlichen Vorteile einer solchen Auswertetechnik hinsichtlich Einfachheit, Schnelligkeit und Zuverlässigkeit brauchen nicht besonders hervorgehoben zu werden. Nach diesem Prinzip können bestimmte Wissenskomplexe, wie mathematische Modelle, vom Fachspezialisten optimal programmiert und danach mit einem Minimum an Vorbildung von Wissenschaftlern und Hilfskräften anderer Fachgebiete als geschlossene Bausteine verwendet werden. Die Prozeduren KORR und TEST sind universelle mathematische Modelle, die ein Biologe, Soziologe, Betriebswirtschaftler oder ein beliebig anderer Fachwissenschaftler ebenso wie ein Chemiker anwenden kann. Speziell ist allein die jeweilige Problemstellung und das danach gestaltete zumeist sehr einfache Rahmenprogramm.

Zusammenfassend zeigen die Abb. 1 und 2 nochmals wesentliche Teile der vorstehenden Gedankengänge.

MATHEMATISCHE STRUKTUR

Grundgrößen und Varianzen

Der Rechengang beginnt mit einer einfachen Summierung der formalen Parameter X und Y, die entsprechend den Funktionsansätzen aus den primären Eingangsgrößen y_i, x_i gebildet werden. Mit den formalen Mittelwerten $\bar{X}$ und $\bar{Y}$ werden danach die n Abweichungen $X - \bar{X}$ und $Y - \bar{Y}$ gebildet und zu varianzähnlichen Ausdrücken VX, VY und VXY aufsummiert.

Tabelle 1 gibt unter [1] und [2] eine Zusammenstellung der Rechenprozesse. Man beachte, daß X und Y keine einfachen Variablen, sondern Felder (Vektoren) aus jeweils n Einzelgrößen bzw. n Kombinationen aus mehreren Einzelgrößen sind.

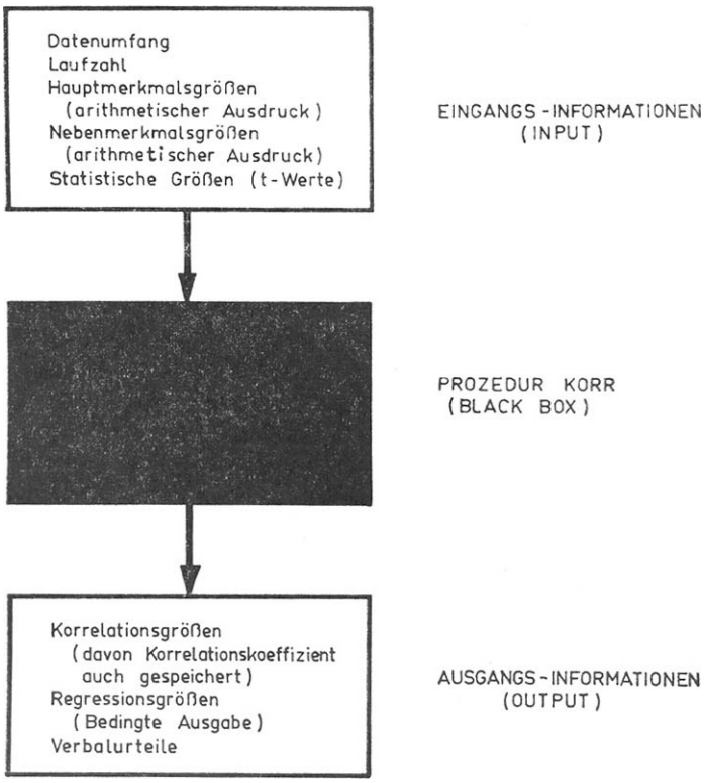


ABB. 1.—INPUT/OUTPUT-System der Prozedur KORR.

ABB. 2.—Programm-Schema zur Durchführung von Korrelationsrechnungen und *r*-Vergleichen für 3 Korrelationsfunktionen.

TABELLE I.—MATHEMATISCHE STRUKTUR DER LINEAREN KORRELATIONSRECHNUNG (FETT GEDRUCKTE SYMBOLE = ALGOL-NAMEN)

1 Grundgrößen	2 Varianzen
$\mathbf{S1} = \frac{1}{n}\sum_1^n \mathrm{X} = \overline{\mathrm{X}}$	$\mathbf{VX} = (n-2)\cdot s_x^2 = \sum_1^n \mathbf{S4} \times \mathbf{S4}$
$\mathbf{S2} = \frac{1}{n}\sum_1^n \mathrm{Y} = \overline{\mathrm{Y}}$	$\mathbf{VY} = (n-2)\cdot s_y^2 = \sum_1^n \mathbf{S5} \times \mathbf{S5}$
$\mathbf{S3} = \frac{1}{n}\sum_1^n \mathrm{X}\cdot\mathrm{X}$	
$\mathbf{S4} = \mathrm{X} - \overline{\mathrm{X}} = \mathrm{X} - \mathbf{S1}$	$\mathbf{VXY} = (n-2)\cdot s_{xy} = \sum_1^n \mathbf{S4} \times \mathbf{S5}$
$\mathbf{S5} = \mathrm{Y} - \overline{\mathrm{Y}} = \mathrm{Y} - \mathbf{S2}$	

3 Korrelationsgrößen
Korrelationskoeffizient: $\mathbf{R} = r_{xy} = \frac{s_{xy}}{s_x \cdot s_y} = \mathrm{VXY}/\sqrt{\mathrm{VX} \times \mathrm{VY}}$
Bestimmtheitsmaß: $\mathbf{B} = r_{xy}^2 = \mathrm{VXY} \times \mathrm{VXY}/(\mathrm{VX} \times \mathrm{VY})$
Prüfgröße: $\mathbf{TAU} = \tau_r = \sqrt{(N-2) \times B/(1-B)}$

4 Regressionsgrößen
Berechnung erfolgt nur für $\tau_r \geqq t_1 \cdot$ (V1 WAHR)
Konstanten: $\mathbf{V} = [V] = \frac{s_{xy}}{s_x^2} = \mathrm{VXY}/\mathrm{VX}$ und $\mathbf{U} = [U] = \overline{\mathrm{Y}} - [V]\cdot\overline{\mathrm{X}} = \mathbf{S2} - \mathrm{V} \times \mathbf{S1}$
Abweichungen: $\mathbf{SK} = [s_K] = s_y \cdot \sqrt{1-B} = \sqrt{\mathrm{VY} \times (1-B)/(N-2)}$
$\mathbf{SV} = [s_V] = \lvert V\rvert/\mathrm{TAU}$ und $\mathbf{SU} - [s_U] = \mathrm{SV} \times \sqrt{\mathbf{S3}}$

5 Boole'sche Variable			6 Urteile
Vergleiche mit t-Werten der t-Verteilung für $f = n-2$ und den Sicherheiten $S = 95\%$: $\mathbf{T1} = t_1$; $S = 99\%$: $\mathbf{T2} = t_2$; $S = 99{,}9\%$: $\mathbf{T3} = t_3$			Wenn V1 nicht wahr: KEINE KORRELATION NACHWEISBAR
V1	WAHR	für $\tau_r \geqq t_1$	Wenn V2 nicht wahr UND V1 wahr: KORRELATION NUR WAHRSCHEINLICH
	NICHT WAHR	für $\tau_r < t_1$	
V2	WAHR	für $\tau_r \geqq t_2$	Wenn V3 nicht wahr UND V2 wahr: KORRELATION SIGNIFIKANT NACHGEWIESEN
	NICHT WAHR	für $\tau_r < t_2$	
V3	WAHR	für $\tau_r \geqq t_3$	Wenn V3 wahr: KORRELATION HOCHSIGNIFIKANT NACHGEWIESEN
	NICHT WAHR	für $\tau_r < t_3$	

Korrelationsgrößen und Regressionsgrößen

Aus den Varianzen folgen unmittelbar der Korrelationskoeffizient r_{xy}, das Bestimmtheitsmaß B und die Prüfgröße τ_r nach den Rechenformeln, die in [3] der Tab. 1 aufgeführt sind.

Sofern überhaupt eine Korrelation nachweisbar ist, werden die Konstanten $[U]$ und $[V]$ der Regressionsgeraden (2) und die Abweichungen $[s_K]$, $[s_U]$, $[s_V]$ nach den

Formeln in [4] der Tab. I berechnet, die aus dem Minimumsansatz

$$\sum_1^n \{[U] + [V] \,.\, X - Y\}^2 = \sum_1^n \nu_i^2 = \text{MINIMUM} \tag{3}$$

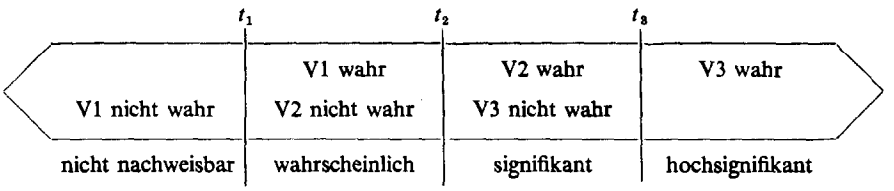
abgeleitet werden können. Einzelheiten siehe Gottschalk.[1]

Boole'sche Variable und Urteile

Der numerische Wert der Prüfgröße τ_r wird mit Werten t der t-Verteilung verglichen, wobei diese Vergleiche durch Zuordnung Boole'scher Variabler in einfache JA/NEIN- oder WAHR/NICHT WAHR-Entscheidungen überführt werden können.

Zur Beurteilung der Realität und Straffheit des Zusammenhanges ist es zweckmäßig, eine vierstufige Urteilsskala heranzuziehen, die sich aus Vergleichen von τ_r mit den Werten t_1; t_2; t_3 für Statistische Aussage-Sicherheiten $S = 95$; 99; 99,9% (level of significance 0,05; 0,01; 0,001) und dem Korrelationsfreiheitsgrad $f = n - 2$ (2 Konstanten) ergeben. Die Integralgrenzen t der t-Verteilung sind in statistischen Tabellenwerken oder Lehrbüchern tabelliert.

In [5] und [6] der Tab. I sind die Boole'schen Variablen und die Urteile formuliert, während nachfolgende Skizze die „Wahrheitstafel" zu [6] verdeutlicht.



Vergleich von Korrelationskoeffizienten

Zum Vergleich von 2 Korrelationskoeffizienten ist eine Prüfgröße λ_r zu bilden und mit den Integralgrenzen λ der Normalverteilung für die Statistischen Sicherheiten $S = 95$; 99; 99,9% (level of significance 0,05; 0,01; 0,001) zu vergleichen. Für die Beurteilung der Unterschiede wird auch hier eine vierstufige Urteilsskala definiert. Die Unterschieds-Wahrheitstafel hat die gleiche Struktur wie die Korrelations-Wahrheitstafel. Einzelheiten der sehr einfachen mathematischen Struktur des λ-Testes sind der Abb. 5 zu entnehmen.

Theoretisch können bei der Durchrechnung von α Korrelationsfunktionen insgesamt

$$\binom{\alpha}{2} = \frac{\alpha!}{2!\,(\alpha - 2)!} = \tfrac{1}{2}\alpha \,.\, (\alpha - 1).$$

verschiedene λ-TESTS durchgeführt werden, sofern dies in jedem Fall sinnvoll erscheint. Ein zumindest wahrscheinlich größerer Korrelationskoeffizient gibt dem betreffenden Funktionsansatz Priorität vor dem anderen Ansatz. Eine solche Priorität ist jedoch problematisch, wenn sie mit einer komplizierten oder gesetzmäßig nicht aufschlüsselbaren Funktion erzielt wird.

PROGRAMMIERUNG

Flußdiagramm

Abbildung 3 zeigt das vollständige Ablaufschema der Prozedur KORR. Die Prozedur TEST ist so einfach, daß ein Flußdiagramm überflüssig ist.

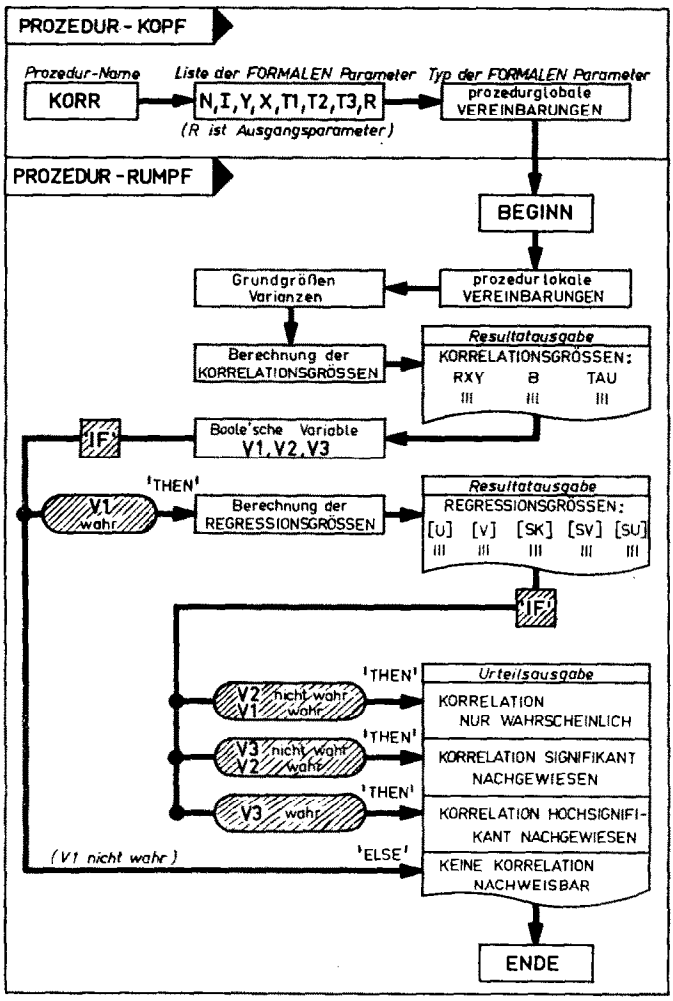


ABB. 3.—Flußdiagramm der ALGOL-Prozedur KORR.

ALGOL-Prozeduren und Rahmenprogramm

Abbildung 4 bringt die ALGOL-Formulierung der Prozedur KORR, während Abb. 5 die mathematische Struktur und die ALGOL-Formulierung der einfachen Prozedur TEST enthält.

Die Prozeduren sind erprobt und brauchen von einem Benutzer nur sorgfältig abgeschrieben und an ein Rechenzentrum gegeben zu werden. Die zukünftige Arbeit besteht im Schreiben eines Rahmenprogrammes, in das die Prozeduren durch Nennung ihres Kenn-Namens im Vereinbarungsteil eingeführt und durch Aufrufe im Anweisungsteil rechnerisch aktiviert werden. Die Schwarzen Kästen der beiden Prozeduren bestehen im ALGOL aus separaten Lochstreifen-Rollen (in Sonderfällen Lochkartenstapel), die im Gegensatz etwa zum Radiogerät sehr schnell vervielfältigt und an andere Interessenten weitergegeben werden können. Bei Schreiben des Datenstreifens mit aktuellen Daten ist lediglich zu beachten, daß die Reihenfolge der Daten mit der Reihenfolge in der Leseanweisung übereinstimmt.

```
'PROCEDURE' KORR (N,I,V,X,T1,T2,T3,R);
    'REAL' Y,X,T1,T2,T3,R;   'INTEGER' N,I;

    'BEGIN'
      'REAL' S1,S2,S3,S4,S5,VX,VY,VXY,B,TAU,U,V,SK,SU,SV;
      'BOOLEAN' V1,V2,V3;

      S1:=S2:=S3:=VX:=VY:=VXY:=0;
      'FOR' I:=1 'STEP' 1 'UNTIL' N 'DO'
        'BEGIN' S1:=S1+X; S2:=S2+Y; S3:=S3+X*X 'END';
      S1:=S1/N; S2:=S2/N; S3:=S3/N;

      'FOR' I:=1 'STEP' 1 'UNTIL' N 'DO'
        'BEGIN' S4:=X-S1; S5:=Y-S2; VX:=VX+S4*S4;
          VY:=VY+S5*S5; VXY:=VXY+S4*S5 'END';

      B:=VXY/VX/(VX*VY); R:=SIGN(VXY)*SQRT(B);
      TAU:=SQRT((N-2)*B/(1-B));
      V1:=TAU 'NOTLESS' T1;
      V2:=TAU 'NOTLESS' T2;
      V3:=TAU 'NOTLESS' T3;

      WRITE ("<=== KORRELATIONSGROESSEN:
             <=␣␣RXY␣␣B␣␣TAU");  PRINT (R,B,TAU);

      'IF' V1 'THEN' 'BEGIN' V:=VXY/VX; U:=S2-V*S1;
                     SK:=SQRT(VY*(1-B)/(N-2));
                     SV:=ABS(V)/TAU;
                     SU:=SV*SQRT(S3);
        WRITE ("<=== REGRESSIONSGROESSEN:
               <=== ␣␣U␣␣V1␣␣SK␣␣SU␣␣SV");
                     PRINT (U,V,SK,SU,SV);

                     WRITE ("<=== KORRELATION");
                     'IF' 'NOT' V2 'AND' V1 'THEN'
                       WRITE ("␣␣NUR␣␣WAHRSCHEINLICH");
                     'IF' 'NOT' V3 'AND' V2 'THEN'
               WRITE ("␣␣SIGNIFIKANT␣␣NACHGEWIESEN");
                     'IF' V3 'THEN'
               WRITE ("␣␣HOCHSIGNIFIKANT␣␣NACHGEWIESEN")
                     'END'
               'ELSE'
        WRITE ("<=== KEINE␣␣KORRELATION␣␣NACHWEISBAR");

    'END' PROZEDUR KORR;
```

ABB. 4.—ALGOL-Formulierung der Prozedur KORR.

MATHEMATISCHE STRUKTUR DES λ-TEST

1. Eingangsparameter $n_1 \geq 3$; $n_2 \geq 3$

   2 Korrelationskoeffizienten $R1 = r_{xy}\,(1)$ aus $N1 = n_1$ Daten
   $R2 = r_{xy}\,(2)$ aus $N2 = n_2$ Daten

2. Prüfgröße

$$L = \lambda_r = \frac{1}{2}\sqrt{\frac{(N1-3)\times(N2-3)}{N1+N2-6}} \times \ln\frac{(1+R1)\times(1-R2)}{(1-R1)\times(1+R2)}$$

3. Boole'sche Variable

   V1 WAHR für $\lambda_r \geq \lambda\,(95)$ / NICHT WAHR für $\lambda_r < \lambda\,(95)$
   V2 WAHR für $\lambda_r \geq \lambda\,(99)$ / NICHT WAHR für $\lambda_r < \lambda\,(99)$
   V3 WAHR für $\lambda_r \geq \lambda\,(99{,}9)$ / NICHT WAHR für $\lambda_r < \lambda\,(99{,}9)$

   wobei $\lambda\,(S)$ = Integralgrenzen der Normalverteilung für
   S = 95 / 99 / 99,9 % Statistischer Sicherheit.
   $\lambda\,(95) = 1{,}960$ / $\lambda\,(99) = 2{,}576$ / $\lambda\,(99{,}9) = 3{,}291$

4. Urteile

   V1 nicht wahr : UNTERSCHIED NICHT NACHWEISBAR
   V2 nicht wahr UND V1 wahr : UNTERSCHIED NUR WAHRSCHEINLICH
   V3 nicht wahr UND V2 wahr : UNTERSCHIED SIGNIFIKANT
   V3 wahr : UNTERSCHIED HOCHSIGNIFIKANT

ALGOL-FORMULIERUNG

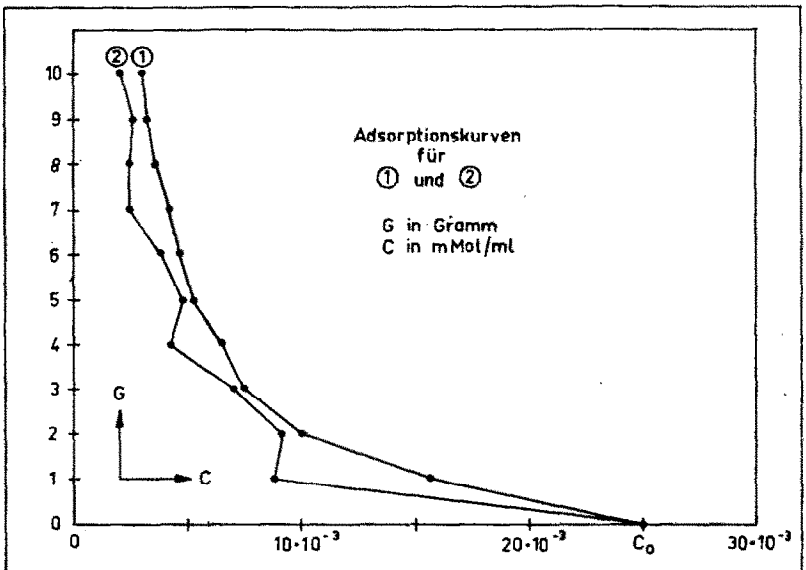
```
'PROCEDURE' TEST (N1,N2,R1,R2);
  'REAL' R1,R2;  'INTEGER' N1,N2;

  'BEGIN' 'REAL' L; 'BOOLEAN' V1,V2,V3;
    'IF' R1 'NOT LESS' 1 'OR' R2 'NOT LESS' 1 'THEN' 'BEGIN'
      WRITE ("<=== TEST␣␣UNBESTIMMT"); 'GO TO' E 'END';
    L:=0,5*SQRT((N1-3)*(N2-3)/(N1+N2-6))
                          *LN((1+R1)*(1-R2)/((1-R1)*(1+R2)));
    WRITE ("<=== LAMBDA="); TYPE (L); L:=ABS(L);
    V1:='NOT LESS' 1,960; V2:='NOT LESS' 2,576; V3:='NOT LESS' 3,291;

    WRITE ("␣␣UNTERSCHIED");
    'IF' 'NOT' V1 'THEN' WRITE ("␣␣NICHT␣␣NACHWEISBAR");
    'IF' 'NOT' V2 'AND' V1 'THEN' WRITE ("␣␣NUR␣␣WAHRSCHEINLICH");
    'IF' 'NOT' V3 'AND' V2 'THEN' WRITE ("␣␣SIGNIFIKANT");
    'IF' V3 'THEN' WRITE ("␣␣HOCHSIGNIFIKANT");
E:  'END' PROZEDUR TEST;
```

ABB. 5.—Mathematische Struktur und ALGOL-Formulierung der Prozedur TEST (fett gedruckte Symbole = ALGOL-Namen).

Im folgenden wird die Erstellung eines speziellen Rahmenprogrammes an einem Beispiel gezeigt.

BEISPIEL

In dem nachfolgenden Beispiel werden nur die für die elektronische Datenverarbeitung erforderlichen Informationen angeführt. Einzelheiten zur Versuchsdurchführung und Folgerung aus den Ergebnissen der Korrelationsrechnung für die Ansätze [11] und [21] siehe Gottschalk[1] (Beispiel 9).



Laufzahl i	1	2	3	4	5	6	7	8	9	10	11
G_i	0,0	1,0	2,0	3,0	4,0	5,0	6,0	7,0	8,0	9,0	10,0
$10^3 \cdot C1_i$	25,00	15,62	10,00	7,46	6,54	5,24	4,63	4,27	3,62	3,25	3,06
$10^3 \cdot C2_i$	25,00	8,85	9,10	7,10	4,20	4,76	3,83	2,49	2,40	2,58	2,03

ABB. 6.—Cl und C2 als Funktion von G (aktuelle Eingangsinformationen).

Problemstellung

In jeweils 10 Untersuchungen wurde die Brauchbarkeit von 2 verschiedenen Adsorptionsmitteln ① und ② zur selektiven Entfernung eines störenden Bestandteiles aus einer Lösung getestet.

Hauptmerkmal (vorgegeben) = Menge G an Adsorptionsmittel ① bzw. ② in Gramm
Merkmalsgrößen $y_i = G_i$ = G[I]

Nebenmerkmal (gefunden) = Restkonzentration C in mMol/ml in der Lösung nach definierter Behandlung von Lösungen mit der Anfangskonzentration $C_0 = 2{,}50 \cdot 10^{-2}$ mMol/ml.

Merkmalsgrößen für ①: $x(1)_i = C1_i$ = C1[I]
②: $x(2)_i = C2_i$ = C2[I]

Abbildung 6 bringt die graphische Darstellung und die Tabelle der aktuellen Daten.

Mathematische Rahmenstruktur

Bei Einbeziehung der Anfangskonzentration $C_0 = C1[1] = C2[1]$ liegen insgesamt $n = N = 11$ Daten mit $i = I = 1, 2, 3, \ldots, 11$ für jede Merkmalsreihe vor.

```
'BEGIN'
  'REAL' T1,T2,T3, R11,R12,R13, R21,R22,R23;
  'INTEGER' I;
  'ARRAY' G, C1, C2 [1:11];

  Einlese - STOP durch hinreichend lange Folge von BU-Zeichen

  'PROCEDURE' KORR (N,I,Y,X,T1,T2,T3,R); ....

  'PROCEDURE' TEST (N1,N2,R1,R2); ....

  dann weiter Rahmenprogramm einlesen

  READ (T1,T2,T3);
  'FOR' I:=1 'STEP' 1 'UNTIL' 11 'DO' READ (G[I], C1[I], C2[I]);

  WRITE ("< = KORRELATIONSRECHNUNG, ADSORPTIONSPROBLEM, N=11");

  WRITE ("< [11] G = [U]+[V]/C1");
      KORR (11,I,G[I],1/C1[I],T1,T2,T3,R11);
  WRITE ("< [12] G = [U]+[V] × C1 × C1");
      KORR (11,I,G[I],C1[I] × C1[I],T1,T2,T3,R12);
  WRITE ("< [13] C1/G = [U]+[V] × C1");
      KORR (11,I,C1[I]/G[I],C1[I],T1,T2,T3,R13);
  WRITE ("< [21] G = [U]+[V]/C2");
      KORR (11,I,G[I],1/C2[I],T1,T2,T3,R21);
  WRITE ("< [22] G = [U]+[V] × C2×C2");
      KORR (11,I,G[I],C2[I]×C2[I],T1,T2,T3,R22);
  WRITE ("< [23] C2/G = [U]+[V] × C2");
      KORR (11,I,C2[I]/G[I],C2[I],T1,T2,T3,R23);

  WRITE ("< VERGLEICH DER R-WERTE");
  WRITE ("< R11 MIT R12:"); TEST (11,11,R11,R12);
  WRITE ("< R11 MIT R13:"); TEST (11,11,R11,R13);
  WRITE ("< R12 MIT R13:"); TEST (11,11,R12,R13);
  WRITE ("< R21 MIT R22:"); TEST (11,11,R21,R22);
  WRITE ("< R21 MIT R23:"); TEST (11,11,R21,R23);
  WRITE ("< R22 MIT R23:"); TEST (11,11,R22,R23);
  WRITE ("< R11 MIT R21:"); TEST (11,11,R11,R21);
  WRITE ("< R12 MIT R22:"); TEST (11,11,R12,R22);
  WRITE ("< R13 MIT R23:"); TEST (11,11,R13,R23);

'END' RAHMENPROGRAMM
```

ABB. 7.—ALGOL-Rahmenprogramm des Beispieles.

Nach dem graphischen Bild ist ein nichtlinearer Zusammenhang zwischen G und C zu erwarten. Die formale Korrelationsfunktion

$$Y = [U] + [V] \times X$$

soll auf folgende aktuelle Funktionen angewendet werden:

Adsorptionsmittel ①	[11]	$G[I] = [U] + [V] \times (1/C1[I])$	mit R11
	[12]	$G[I] = [U] + [V] \times C1[I] \times C1[I]$	mit R12
	[13]	$C1[I]/G[I] = [U] + [V] \times C1[I]$	mit R13

Adsorptionsmittel ② [21] G[I] = [U] + [V] × (1/C2[I]) mit R21

[22] G[I] = [U] + [V] × C2[I] × C2[I] mit R22

[23] C2[I]/G[I] = [U] + [V] × C2[I] mit R23

Die Beziehungen [13] und [23] lassen sich leicht in die Langmuir'sche Adsorptionsisotherme überführen. Durch Umformung folgt:

$$G = \frac{C}{[U] + [V] \cdot C} \sim CO \qquad \text{(Oberflächenkonzentration)}$$

Von den 15 möglichen Vergleichen der 6 Korrelationskoeffizienten sind 9 Vergleiche sinnvoll und zwar:

R11 mit R12	R21 mit R22	R11 mit R21
R11 mit R13	R21 mit R23	R12 mit R22
R12 mit R13	R22 mit R23	R13 mit R23

Als t-Werte entnimmt man für $f = n - 2 = 9$ den Tabellen:

$$t_1 = T1 = 2{,}26 \quad (95\%)$$
$$t_2 = T2 = 3{,}25 \quad (99\%)$$
$$t_3 = T3 = 4{,}78 \quad (99{,}9\%)$$

ALGOL-Rahmenprogramm

Im Rahmenprogramm werden namentlich nur die aktuellen Größen

T1, T2, T3, R11, R12, R13, R21, R22, R23, I, G[I], C1[I], C2[I]

vereinbart und soweit sie Eingangs-Informationen darstellen auch eingelesen; n = N = 11 wird direkt numerisch eingesetzt.

Abbildung 7 zeigt das Rahmenprogramm mit den einmaligen Prozedurvereinbarungen, den schriftlichen Erläuterungen durch WRITE-Anweisungen und den insgesamt 15 Prozeduraufrufen. Entsprechend den formulierten Leseanweisungen sind die aktuellen Eingangsdaten in der Reihenfolge

$$\langle t_1, t_2, t_3, G_1, C1_1, C2_1, G_2, C1_2, C2_2, \ldots G_{11}, C1_{11}, C2_{11} \rangle$$

im Datenstreifen numerisch aufzulisten.

Resultate, Urteile, Bearbeitungszeiten

Tabelle 2 gibt eine Zusammenstellung der gerundeten Resultate, während Abb. 8 Anfang, Mittelteil und Ende des von einer Rechenanlage ZUSE Z23 ausgedruckten Ergebnis-Bogens zeigt. Die Durchrechnung des Beispieles erfolgte mit einer relativ

TABELLE II.—ZUSAMMENSTELLUNG DER RESULTATE (GERUNDET)

Korrelationsrechnungen

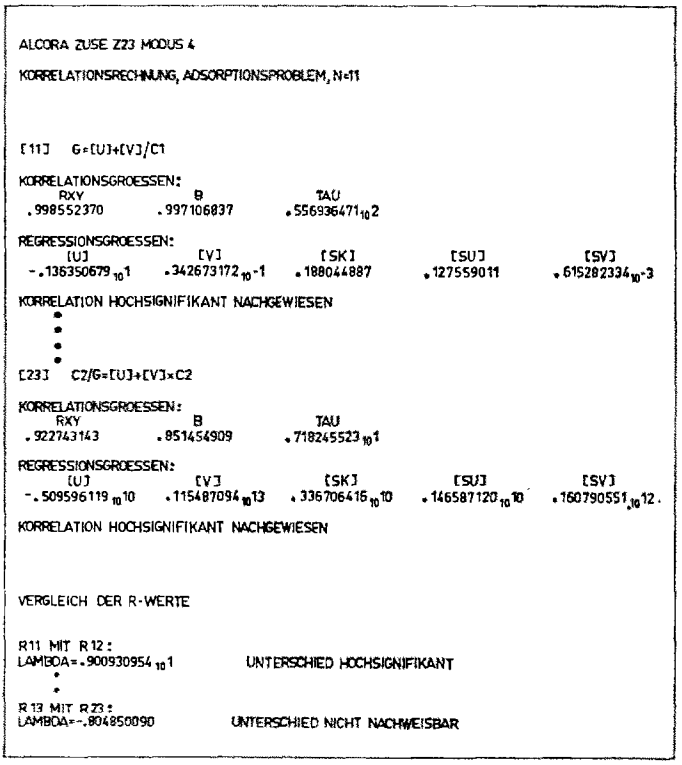
FUNK-TION	[11]	[12]	[13]	[21]	[22]	[23]
Y	G	G	Cl/G	G	G	C2/G
X	1/Cl	Cl^2	Cl	1/C2	$C2^2$	C2
r_{xy}	+0,9986	−0,7112	+0,8351	+0,9712	−0,6151	+0,9227
B	0,9971	0,5058	0,6974	0,9433	0,3784	0,8515
τ_r	55,694	3,035	4,554	12,237	2,341	7,182
[U]	−1,364	+6,352	$-5,80 \cdot 10^9$	−0,495	+5,932	$-5,10 \cdot 10^9$
$[s_U]$	±0,128	±0,864	$\pm 2,33 \cdot 10^9$	±0,514	±0,921	$\pm 1,47 \cdot 10^9$
[V]	+0,03427	$-1,27 \cdot 10^4$	$+1,03 \cdot 10^{12}$	+0,02150	$-1,12 \cdot 10^4$	$+1,15 \cdot 10^{12}$
$[s_V]$	±0,00062	$\pm 0,42 \cdot 10^4$	$\pm 0,23 \cdot 10^{12}$	±0,00176	$\pm 0,48 \cdot 10^4$	$\pm 0,16 \cdot 10^{12}$
$[s_R]$	±0,188	±2,46	$\pm 4,81 \cdot 10^9$	±0,832	±2,76	$\pm 3,37 \cdot 10^9$
Urteil	KHS	KW	KS	KHS	KW	KHS

KKN = Keine Korrelation nachweisbar
KW = Korrelation nur wahrscheinlich
KS = Korrelation signifikant
KHS = Korrelation hochsignifikant

Vergleich der r_{xy} — Werte

	[11]	[12]	[13]	[21]	[22]	[23]
[11]		UHS	UHS	US	—	—
[12]			UNN	—	UNN	—
[13]				—	—	UNN
[21]					UHS	UNN
[22]						UNN

UNN = Unterschied nicht nachweisbar
(UW) = Unterschied nur wahrscheinlich
US = Unterschied signifikant
UHS = Unterschied hochsignifikant



```
ALCORA ZUSE Z23 MODUS 4

KORRELATIONSRECHNUNG, ADSORPTIONSPROBLEM, N=11


[11]   G=[U]+[V]/C1

KORRELATIONSGROESSEN:
     RXY                B                TAU
 .998552370         .997106037       .556936471 10 2

REGRESSIONSGROESSEN:
      [U]               [V]              [SK]             [SU]             [SV]
 -.136350679 10 1   .342673172 10 -1   .188044887       .127559011       .615282334 10 -3

KORRELATION HOCHSIGNIFIKANT NACHGEWIESEN
      .
      .
      .
      .
[23]   C2/G=[U]+[V]×C2

KORRELATIONSGROESSEN:
     RXY                B                TAU
 .922743143         .851454909       .718245523 10 1

REGRESSIONSGROESSEN:
      [U]               [V]              [SK]             [SU]             [SV]
 -.509596119 10 10  .115487094 10 13  .336706416 10 10  .146587120 10 10  .160790551 10 12 .

KORRELATION HOCHSIGNIFIKANT NACHGEWIESEN


VERGLEICH DER R-WERTE

R11 MIT R12:
LAMBDA=.900930954 10 1          UNTERSCHIED HOCHSIGNIFIKANT
      .
      .
R13 MIT R23:
LAMBDA=-.804850090              UNTERSCHIED NICHT NACHWEISBAR
```

ABB. 8.—Ausschnitt des maschinell erstellten Ergebnis-Bogens.

langsamen Klein-Rechenanlage ZUSE Z23, wobei folgende Kenngrößen ermittelt wurden:

Angezeigte Rechenbefehle im Befehlsregister für das Gesamtprogramm: 1 508			
Einlesen der Prozedur KORR	: 1 min	40 sec	
Einlesen der Prozedur TEST	:	43 sec	
Einlesen des Rahmenprogrammes	: 2 min	53 sec	
PROGRAMM-EINLESEZEIT PEZ	: 5 min	16 sec	
Daten-Einlesezeit DEZ	:	16 sec	
Rechenzeit (Schnell-Locher-Ausgabe) RZ	: 3 min	26 sec	(bei Direktausgabe aber 9 min 44 sec)
ELEKTRONISCHE BEARBEITUNGSZEIT EBZ:	3 min	42 sec	
GESAMTZEIT für das Beispiel	: 8 min	58 sec	

Für die vollständige Durchrechnung und Beurteilung von nur einer der 6 Korrelationsfunktionen werden nur etwa 30 sec RZ benötigt. Die Ausgabe über

Schnell-Locher liefert einen Ergebnis-Lochstreifen, der mit jedem ALGOL-Schreiber beliebig oft in Klarschrift-Bögen nach Abb. 8 umgesetzt werden kann. Die Umsetzungszeit beträgt 5 min 42 sec. Dieses Vorgehen bietet gegenüber der langsamen direkten Klarschrift-Ausgabe den Vorteil einen wesentlichen Verkürzung der Maschinen-Belegungszeit, da in der Z23-Anlage die Rechenprozesse während des Druckvorganges unterbrochen werden.

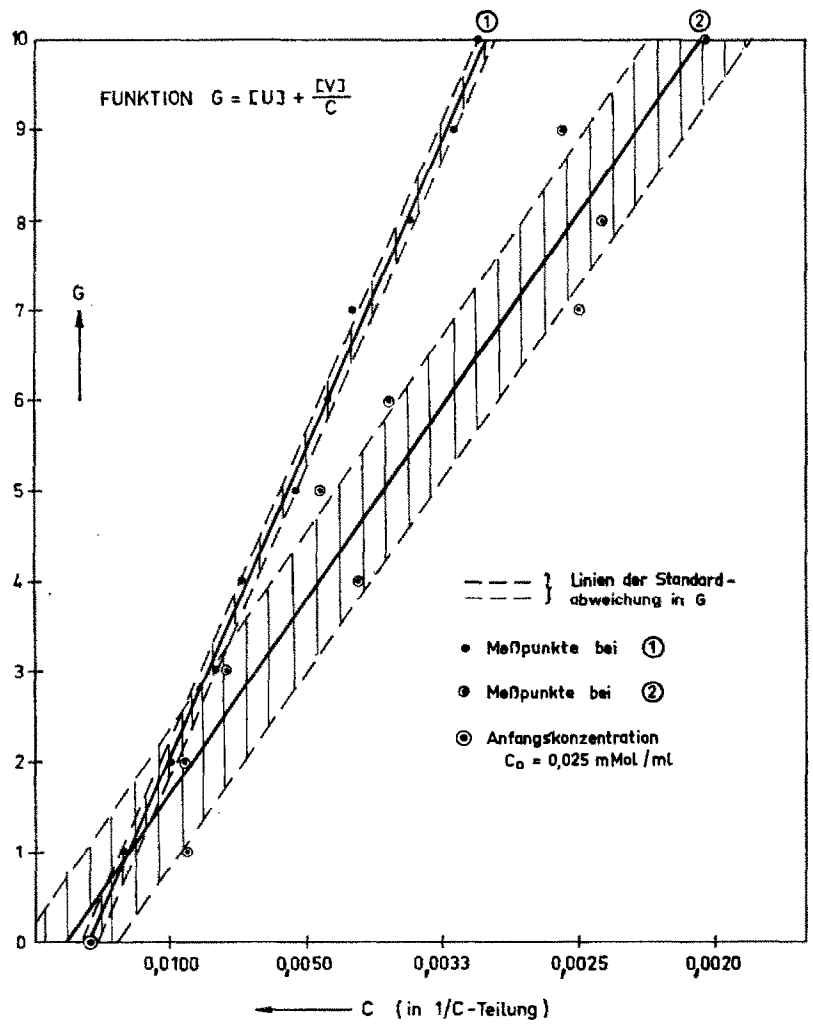


ABB. 9—Regressionsgeraden und Meßpunkte.

Bei konventioneller Rechentechnik mit Tischrechnern benötigt auch ein geübter menschlicher Rechner für das Beispiel mindestens 15 Stunden = 900 min (2 bis 3 Arbeitstage) zu einer gleichartigen Durchrechnung und Urteilsbildung, was einem Zeitfaktor von über 100 entspricht. Es sei erwähnt, daß bereits mit neueren mittelgroßen Rechenanlagen die Gesamtzeit durchaus auf weniger als 1 min vermindert werden kann.

Diskussion der Ergebnisse

Die aktuellen Daten werden am besten durch die strukturell gleichartigen Funktionen [11] und [21]

$$G = [U] + \frac{[V]}{C}$$

beschrieben, wobei die Standardabweichung in G bei [11] mit $[s_K] = \pm 0{,}19$ g wesentlich kleiner als bei [21] mit $[s_K] = \pm 0{,}83$ g ist. Die Konstante $[V]$ (Steigung der Regressionsgeraden) stellt ein Maß des Adsorptionsvermögens A dar. A ist umso größer je kleiner $[V]$ ist.

$$A = \frac{1}{[V]} \qquad \text{in } g^{-1}.\ (\text{mMol/ml})^{-1}$$

Im vorliegenden Beispiel besitzt das Adsorptionsmittel ② mit $A2 = 46{,}5$ ein höheres Absorptionsvermögen als ① mit $A2 = 29{,}2$. Wegen der in $[s_K]$ erkennbaren sehr viel größeren „Dosier-Streuung" von ② gegenüber ① wird man aber dem Adsorptionsmittel ① wegen „besserer Gleichmäßigkeit" zumeist den Vorzug geben. Der Vergleich von R11 mit R21 ergibt, daß das Datenmaterial von ① signifikant besser als dasjenige von ② korreliert ist. Abbildung 9 zeigt im 1/C; G-Diagramm die beiden Regressionsgeraden und die gefundenen Meßpunkte.

Für die Funktionen [12] und [22] vom Typ

$$G = [U] + [V] \cdot C^2$$

ist eine Korrelation nur wahrscheinlich. Wie auch die extrem großen Standardabweichungen $[s_K]$ zeigen, sind sie ungeeignet zur Interpretation des vorliegenden Datenmaterials. Die Unterschiede von R11 zu R12 bzw. von R21 zu R22 sind zudem hochsignifikant. Die Langmuir-ähnlichen Funktionen [13] und [23] vom Typ

$$\frac{C}{G} = [U] + [V] \cdot C \qquad \text{bzw. umgeformt} \qquad G = \frac{C}{[U] + [V] \cdot C}$$

ergeben zwar eine signifikante bzw. hochsignifikante Korrelation, besitzen aber gegenüber den Funktionen [11] und [21] einen kleineren Korrelationskoeffizienten. Zwischen R11 und R13 ist der Unterschied hochsignifikant, während zwischen R21 und R23 ein solcher nicht nachweisbar ist. Auf weitere Analysen der Auswertungsergebnisse kann hier nicht eingegangen werden. Die Ergebnisse der Korrelationsrechungen bilden die Planungsgrundlage für weitere gezielte Untersuchungen. Die sodann anfallenden Resultate werden zweckmäßig nach verfeinerten Methoden, insbesondere Ausgleichsrechnungen, aufgeschlüsselt, wie in nachfolgenden Arbeiten gezeigt werden soll.

Summary—The variable experimental parameters for similar objects or processes can be connected by means of relationships that in the first instance may be unknown. The reality and rigour of the connection of data series in the framework of given correlation functions can be checked by the statistical methods of interpreting correlations. In this paper the mathematical details of the necessary calculations are given and formulated in ALGOL language as universally applicable subprogramme procedures called KORR and TEST. It is shown that such universal procedures correspond to "black boxes" in cybernetic terminology, and can be used as building blocks, without knowledge

of their mathematical content. The writing of an overall programme for special problems is thereby so essentially simplified that it can be done satisfactorily after a short training without a mathematical background. As a practical example, 6 correlation equations and 9 sets of correlation coefficients can be programmed and solved electronically in 9 min. The time taken by conventional methods is 100 times as great.

Résumé—On peut relier les paramètres expérimentaux variables pour des objets ou des procédés similaires au moyen de relations qui, en première instance, peuvent être inconnues. La réalité et la rigueur de la liaison entre des séries de données dans le cadre de fonctions de corrélation données peuvent être contrôlées par les méthodes statistiques d'interprétation de corrélations. Dans ce mémoire on donne les détails mathématiques des calculs nécessaires, et les formule en langage ALGOL à l'état de techniques de sub-programme universellement applicables, appelées KORR et TEST. On montre que de telles techniques universelles correspondent aux "boîtes noires" en terminologie cybernétique et peuvent être utilisées comme des blocs de construction, sans connaissance de leur contenu mathématique. L'écriture d'un programme global pour des problèmes spéciaux est de ce fait tellement simplifiée qu'elle peut être faite de façon satisfaisante après un court entraînement sans un fond de connaissances mathématiques. A titre d'exemple pratique, 6 équations de corrélation et 9 ensembles de coefficients de corrélation peuvent être programmés et résolus électroniquement en 9 mn. Le temps nécessité par les méthodes ordinaires est 100 fois plus long.

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SHORT COMMUNICATIONS

The platinum–20% rhodium electrode in potentiometry

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POTENTIOMETRIC technique with metal/metal oxide electrodes has been developed in great detail, but alloy electrodes have not been so thoroughly studied. The platinum–rhodium alloy electrode (10–40% Rh) has attracted some attention,[1,2] but complete information is not available. Potentials are taken with a stainless steel electrode in some solutions,[3] though mostly in the study of corrosion.[4] With a view to studying the effect of alloying on the electrode potential, we used the platinum–rhodium electrode in various redox and acid–base titrations.

EXPERIMENTAL

The vernier potientiometer used was manufactured by the Oriental Science Apparatus Workshop, Ambala, India and was capable of measuring 10^{-7} V. Platinum and platinum–20% rhodium electrodes were prepared by fusing the 19 s.w.g. wires into 5-mm bore soft glass tubing. A dip-type

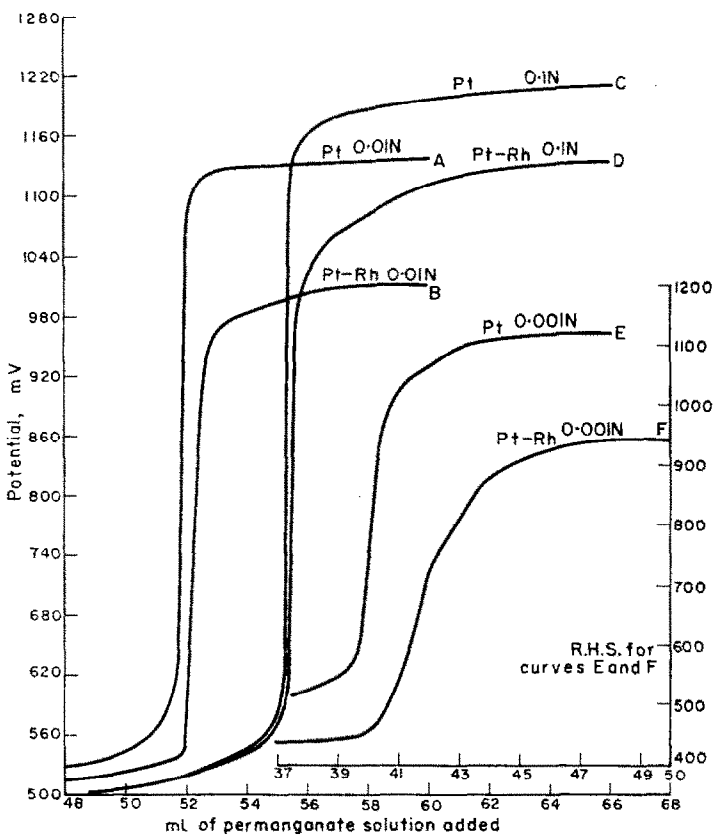

FIG. 1.—Redox titrations of 0·1, 0·01 and 0·001*N* iron(II) and permanganate, with Pt/S.C.E. and Pt–Rh/S.C.E. electrode systems.

TABLE I.—PERFORMANCE OF Pt–20% Rh ALLOY ELECTRODE IN REDOX AND ACID–BASE TITRATIONS, COMPARED WITH THAT OF THE PLATINUM ELECTRODE (S.C.E. REFERENCE ELECTRODE)

Titrant	Titrand	Normality	End-point, *ml* Pt	End-point, *ml* Pt/Rh	Difference, *ml*	Wave-height, *mV* Pt	Wave-height, *mV* Pt/Rh	Difference, *mV*	Remarks
Cerium(IV) sulphate	Iron(II) sulphate	0·1	55·52	55·76	+0·24	519	486	33	Pt/Rh curve deformed
		0·01	44·54	44·68	+0·14	534	462	72	
		0·001	25·15	25·40	+0·25	454	147	207	
Potassium dichromate	Iron(II) sulphate	0·1	7·04	7·02	−0·02	642	93	549	Pt/Rh curve is deformed
		0·01	26·40	26·40	0·00	404	81	323	
Iron(II) sulphate	Potassium permanganate	0·1	55·38	55·48	+0·10	630	500	130	Pt/Rh curve is deformed
		0·01	51·82	52·14	+0·32	576	441	135	
		0·001	40·60	41·65	+0·05	541	450	91	
Sodium hydroxide	Sulphuric acid	0·1	54·52	54·42	−0·10	265	150	115	Both waves are well formed
		0·01	56·40	56·30	−0·10	270	93	117	
		0·001	—	—					No noticeable rise obtained with either electrodes.

saturated calomel electrode (S.C.E.) was used. The metal electrodes were cleaned cathodically by electrolysis of 50% v/v sulphuric acid at 0·2 A for 20 min with a platinum anode and the electrode as cathode.

All the chemicals used were either Merck G.R. grade or B.D.H. AnalaR grade. Approximately 0·1*N* solutions of iron(II) ammonium sulphate, potassium permanganate, cerium(IV) sulphate, sodium hydroxide and sulphuric acid were prepared, standardized in the usual way, suitably diluted, and used in suitable combination for titrations.

RESULTS AND DISCUSSION

Redox titrations

Malmstadt and Fett used a Pt–10% Rh electrode for 0·1*N* iron(II)–dichromate and iron(II)–cerium(IV) titrations.[1] They reported good results, though the end-point obtained with the alloy electrode was always later than that with the platinum electrode, by 0·866 and 0·822 ml respectively.

We performed a wide range of redox titrations at various concentrations for the Pt/S.C.E. and Pt–20%(Rh)/S.C.E. systems, as shown in Table I. For 0·1, 0·01 and 0·001*N* iron(II)–cerium(IV) titrations, the end-points with the alloy electrode were always later than with the platinum electrode. Deformities occur in the lower concentration curves for the alloy electrode, and the potential breaks obtained are also less than with the conventional electrode, the difference being 33, 72 and 207 mV for 0·1, 0·01 and 0·001*N* concentrations respectively.

For 0·1 and 0·01*N* dichromate–iron(II) titrations, the end-points are nearly the same for both the electrodes, but the potential breaks for the alloy electrode are smaller than those for platinum by 549 and 323 mV. For 0·1, 0·01 and 0·001*N* iron(II)–permanganate titrations, a similar trend of progressive diminution in potential breaks and of deformities in the lower concentration curves (Fig. 1) is obtained.

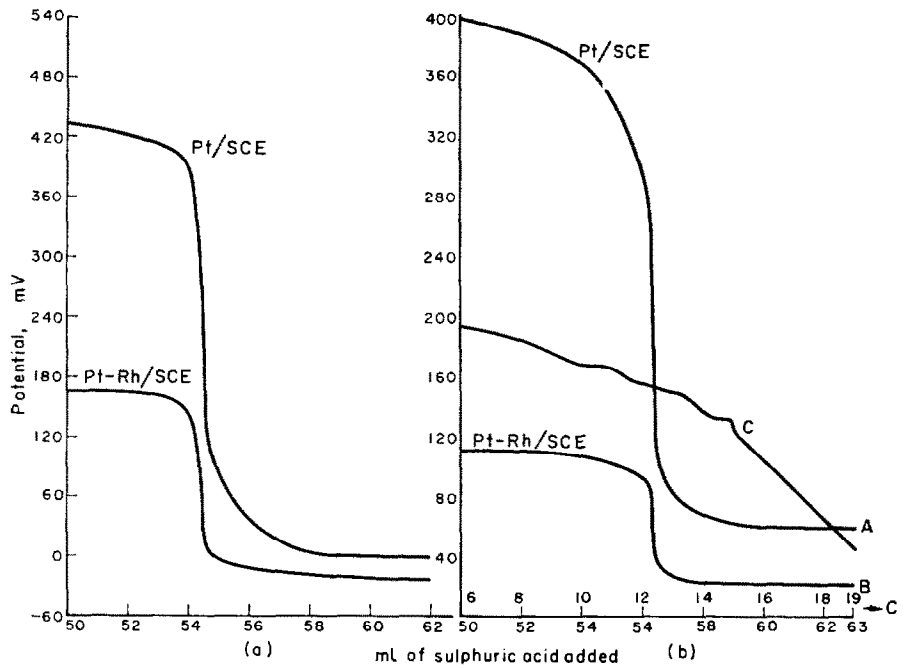

FIG. 2.—Potentiometric acid–base titrations, with Pt/S.C.E. and Pt–Rh/S.C.E. electrode systems.

(*a*) 0·1*M* NaOH *vs.* 0·1*N* H_2SO_4.

(*b*) 0·01*M* NaOH *vs.* 0·01*N* H_2SO_4; curve C is for 0·001*M* NaOH *vs.* 0·001*N* H_2SO_4, with the glass electrode–calomel electrode system.

Acid–base titrations

Strong acid–strong base titrations using the Pt/S.C.E. system have been reported,[5] and the Pt–Rh/S.C.E. system[3] for higher concentrations. The end-points obtained with the alloy electrode are earlier than those with the platinum electrode (Table I). The potential breaks are smaller for the alloy electrodes as usual. No good curves were obtained for any electrode system for concentrations below 0·01*N*. Figure 2 shows the curves for 0·1 and 0·01*N* sodium hydroxide–sulphuric acid titrations for both the electrode systems; results are more reproducible with the platinum electrode than with the alloy electrode.

Bimetallic electrode system

The alloy electrode is, however, found to be very useful in redox and acid–base titrations if used in combination with a platinum electrode. This combination gives peaks which are similar to the first differential peak of the zero current potentiometric curve because the potential breaks obtained at the end-points with these two electrodes, used separately, are different. The peaks could also be calculated from the difference of potential for each point in the iron(II)–permanganate curves shown in Fig. 1. The peaks thus calculated, as well as those actually obtained by using the bimetallic electrode system, are shown in Fig. 3.

Calculated and experimental results obtained for 0·1, 0·01 and 0·001*N* iron(II)–permanganate titrations, with the bimetallic electrode system, are given in Table II. The end-points obtained from the peaks coincide with the true end-points and are exactly the same for all the titrations. As the concentration decreases, the peaks become broader (the observed peaks are much broader than the calculated ones). The increase in peak height with decreasing concentration is greater for the observed

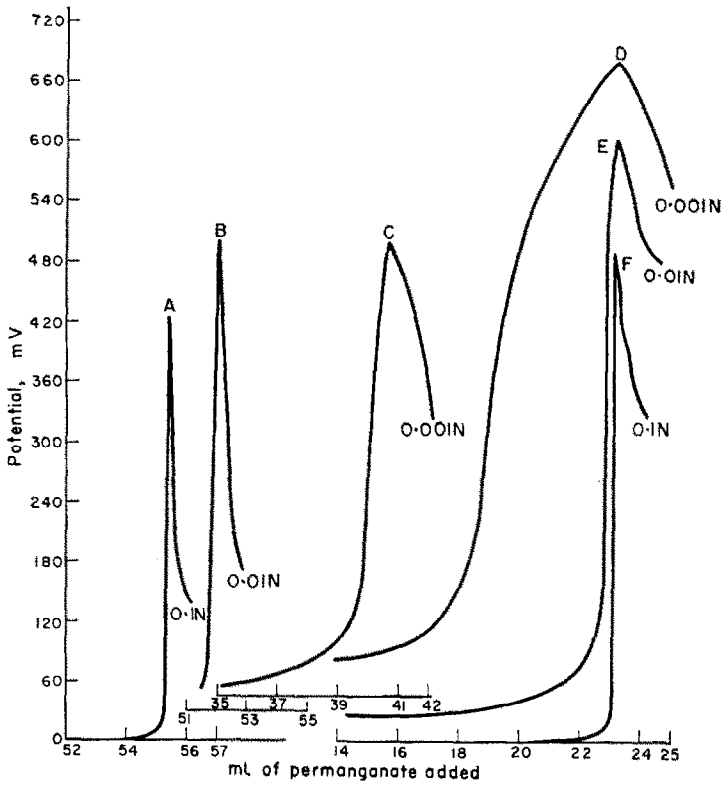

FIG. 3.—Bimetallic electrodes (Pt and Pt–Rh) in the potentiometric titration of iron(II) with permanganate.
Curves A, B, C are calculated from the curves in Fig. 1; curves D, E, F are those observed experimentally.

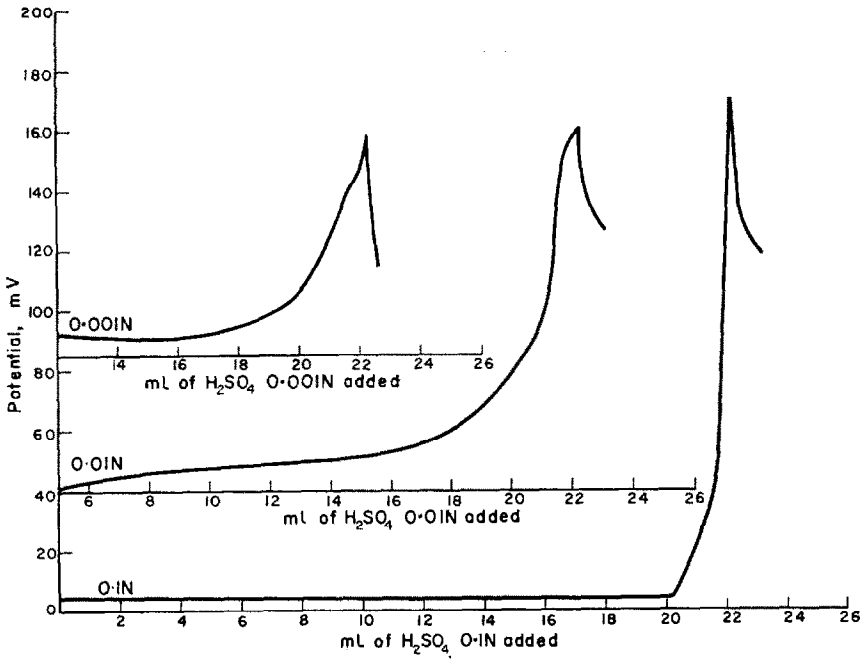

FIG. 4.—Bimetallic electrodes (Pt and Pt–Rh) in the potentiometric titration of NaOH with H_2SO_4.

peaks than for the calculated peaks. This difference in behaviour may be ascribed to meter-induced polarization of the metal and alloy electrodes.[6]

For acid–base titrations however (Fig. 4, Table II) the peak heights decrease with decreasing concentration; the end-points are the true end-points. Excellent peaks were obtained for 0·001*N* solutions, where the Pt/S.C.E., Pt–Rh/S.C.E. or glass/S.C.E. systems fail.

Unlike some bimetallic electrode systems with which an S-shaped curve is obtained,[7,8] this electrode system gives high peaks even at low concentrations, enabling easier true end-point detection.

Smaller potential breaks are obtained with the alloy electrode. Sometimes the end-points are later than the true end-points. In this respect, the alloy electrode is comparable to unclean and untreated metal electrodes which always show a response lag.[9,10] The alloyed and unalloyed bimetallic

TABLE II.—PERFORMANCE OF THE BIMETALLIC ELECTRODE SYSTEM

Titration	Reagent concentration, *N*	Peak height, *mV*		End-point, *ml*		
		Calculated	Observed	True	Calculated	Observed
Iron(II)–permanganate	0·1	426		55·38	55·40	
	0·01	482		51·82	52·00	
	0·001	447		40·60	40·60	
	0·1		489	23·15		23·15
	0·01		579	23·15		23·15
	0·001		600	23·15		23·15
Sodium hydroxide–sulphuric acid	0·1		146	22·28		22·28
	0·01		110	22·29		22·29
	0·001		56	22·29		22·30

system behaves as if it is a combination of unclean and clean platinum electrodes. It has also been observed that the untreated platinum electrode behaves like a platinum–rhodium electrode, though the potentials obtained with it are not as reproducible.

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Summary—The performance of a platinum–20% rhodium alloy indicator electrode is studied in a number of potentiometric redox and acid–base titrations and compared with that of the conventional platinum electrode. The potential breaks obtained with the alloy electrode are always smaller than those obtained with the platinum electrode. The end-points are also usually indicated later than the true end-points. The bimetallic electrode system comprising platinum and platinum–rhodium electrodes gives a peak at the correct end-point even with 0·001*N* concentration titrations, where the ordinary potentiometric systems do not always give good results.

Zusammenfassung—Das Verhalten einer Indikatorelektrode aus einer Legierung von Platin mit 20% Rhodium wird bei einer Anzahl potentiometrischer Redox- und Säure–Basen-Titrationen untersucht und mit dem der gebräuchlichen Platinelektroden verglichen. Die Potentialsprünge mit der legierten Elektrode sind stets kleiner als die mit der Platinelektrode erhaltenen. Die Endpunkte werden gewöhnlich später angezeigt als die wahren Endpunkte. Das Zwei-Metall-Elektrodensystem aus Platin- und Platin-Rhodium-Elektroden gibt am richtigen Endpunkt selbst bei Titrationen mit der Konzentration 0,001*N* eine Spitze, wo die gewönnlichen potentiometrischen Systeme nicht immer gute Ergebnisse zeigen.

Résumé—On a étudié le fonctionnement d'une électrode indicatrice en alliage platine-20% rhodium pour un certain nombre de titrages potentiométirques redox et acide–base et l'a comparé à celui de l'électrode de platine usuelle. Les brisures de potentiel obtenues avec l'électrode en alliage sont toujours plus petites que celles obtenues avec l'électrode de platine. Les points de fin de dosage sont aussi indiqués habituellement plus tard que les points de fin de dosage vrais. Le système d'électrodes bimétallique comprenant des électrodes en platine et platine-rhodium donne un pic au point de fin de dosage correct même avec des titrages à la concentration 0,001*N*, ou les systèmes potentiométriques ordinaires ne donnent pas toujours de bons résultats.

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Neutron-activation analysis of manganese in polysulphide materials*

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As a result of our continuing efforts to apply neutron-activation analysis (NAA) to various matrices containing a variety of elements which are not easily determined by other techniques, we have developed a method for determining manganese in polysulphide adhesives. Manganese, as manganese dioxide, is added to these adhesives as a catalyst, and the "curing rate" is dependent on its concentration. Wet chemical determination of manganese in these samples can be tedious and time-consuming, whereas neutron-activation analysis provides speed and sensitivity, and is non-destructive.

The use of neutron-activation analysis to determine manganese in various materials has been reported by other authors.[1,2] The cross-section (13 barns) and the half-life (2·58 hr) are an ideal combination for analysis in the absence of interfering elements.

EXPERIMENTAL

Apparatus

γ-counting. TMC 400-channel analyser with 3 × 3 in. sodium iodide crystal (T1 activated)

Reactor. The Sandia Engineering Reactor Facility (SERF), with a thermal flux of approximately 2×10^{12} n cm^{-2} sec^{-1}.

Polyethylene rabbits.

Reagents

Manganese metal. United Mineral & Chemical Corp.

Manganese dioxide, C. P. grade.

Coast Pro Seal 890 *polysulphide adhesive.*

Compounded polysulphide standard (2·56% *Mn*). Add a known amount of MnO_2 to pure polysulphide material, mix well and allow to harden.

Procedure

Samples of the standard material, pure manganese metal, and manganese dioxide were irradiated in SERF for times ranging from 5 min to 2 hr and then allowed to "cool" for approximately 30 min. The nuclear reaction used was $^{55}Mn(n, \gamma)^{56}Mn$. Manganese-56 has a half-life of 2·58 hr and decays with emission of 0·845, 1·81, and 2·12-MeV gamma rays. To obtain analytical information, the net counts for the 0·845-MeV photopeaks of the standard material, the manganese metal, and the manganese dioxide were intercompared. No differences were found and any of these three materials could therefore be used as standards. These results were verified by intercomparing the net counts for both the 1·81- and 2·12-MeV photopeaks of these three materials. All three were used as standards for manganese polysulphide unknowns and no significant difference was found in the final results. An irradiation time of 20 min was found to be quite sufficient for determining manganese in the unknowns.

RESULTS AND DISCUSSION

The gamma-ray spectra for our irradiated samples were identical with the standard spectra for ^{56}Mn presented by Heath.[3]

The accuracy and precision of this method were determined by doing two sets of 56 analyses of the standard material (2·56% Mn). The results showed the standard material contained 2·56% of manganese (standard deviations 0·07% and 0·08% Mn). The 0·845-MeV photopeak of ^{56}Mn was used in all cases.

As noted previously, the cross-section of ^{55}Mn and the half-life of ^{56}Mn make an ideal combination for analysis in the absence of interfering elements. However, the application of this method to less favourable sample systems would require the analyst to determine whether there were any serious interferences from radionuclides of other elements in the sample.

* This paper was presented at the Southwest Regional American Chemical Society Meeting, Nuclear and Radiochemistry Section, Albuquerque, New Mexico, 30 November–2 December 1966.

With the irradiation conditions used (20-min irradiation at 2×10^{10} n cm^{-2} sec^{-1}, 30-min preliminary decay time), 1 μg of manganese can be determined. With a 24-hr irradiation and other irradiation conditions remaining constant, 80 ng of manganese could, theoretically, be determined.

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Summary—A fast non-destructive neutron-activation analysis method has been developed for manganese in polysulphide adhesives. Samples are irradiated for 20 min at a thermal flux of 2×10^{10} n cm^{-2} sec^{-1}. The net activity in the 0·845-MeV gamma peak of ^{56}Mn produced by the (n, γ) reaction in the sample is compared with the activity obtained from a weighed amount of pure manganese irradiated at the same time. Samples containing 2–3% of manganese have been analysed with a relative standard deviation of 2·9%.

Zussamenfassung—Eine schnelle zerstörungsfreie neutronenaktivierungsanalytische Methode zur Bestimmung von Mangan in Polysulfidklebern wurde entwickelt. Die Proben werden 20 min bei einem thermischen Fluß von $2 \cdot 10^{10}$ n cm^{-2} sec^{-1} bestrahlt. Die Nettoaktivität im 0,845 MeV-Gammapeak des durch die (n,γ)-Reaktion in der Probe gebildeten ^{56}Mn wird mit der Aktivität verglichen, die man in einer gleichzeitig bestrahlten gewogenen Menge reinen Mangans erhält. 2–3% Mangan enthaltende Proben wurden mit einer relativen Standardabweichung von 2,9% analysiert.

Résumé—On a élaboré une méthode rapide non destructive d'analyse par activation de neutrons pour le manganèse dans des adhésifs polysulfures. Les échantillons sont irradiés pendant 20 mn à un flux thermique de 2×10^{10} n cm^{-2} sec^{-1} On compare l'activité globale du pic gamma 0,845-MeV du ^{56}Mn produit par la réaction (n, γ) dans l'échantillon à l'activité obtenue à partir d'une quantité pesée de manganèse pur irradié au même moment. On a analysé des échantillons contenant 2–3% de manganèse avec un écart type relatif de 2,9%.

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Amperometric titrations of cobalt(II) with hexacyanoferrate(III) in ammonium citrate and glycine media

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THE potentiometric titration of cobalt(II) with hexacyanoferrate(III) in the presence of complexing agents such as ammonia, ethylenediamine, triethylenetetramine, tetraethylenepentamine, glycine, and mixtures of alanine or phenylalanine with glutamic acid, has been described by a number of workers,[1–14] but polarographic studies have not so far been made. In the present communication amperometric titrations of cobalt(II) with hexacyanoferrate(III) in aqueous ammonium citrate and glycine media are reported.

Reagents

Cobalt(II), hexacyanoferrate(III), and other electrolyte solutions were prepared in doubly distilled water. Their strengths were determined by the usual methods.

Ammonium citrate buffer, pH 9·8, was prepared by adding 150 ml of 14·0*M* ammonia to 50 g of citric acid and diluting to one litre.

Glycine buffer was prepared from a 2·8*M* solution of the reagent adjusted to pH 8·0 with potassium hydroxide.

Apparatus

A Heyrovsky Lp-55A manually operated polarograph was used with a Pye Scalamp galvanometer. The capillary characteristics in closed circuit at 0·0 V *vs.* the S.C.E. were $m = 0{\cdot}0035$ g/sec, $t = 4{\cdot}30$ sec per drop.

Procedure

Amperometric titrations in ammonium citrate medium (pH 9·8) were carried out at −0·30 V and −1·55 V (lying on the plateaux of the polarograms of 0·005*M* hexacyanoferrate(III) and 0·005*M* cobalt chloride respectively, both in 0·05*M* potassium chloride). In the glycine medium (pH 8·0) the corresponding potentials used were −0·55 V and −1·5 V.

Both direct (0·2–29·5 mg of cobalt(II) in the cell) and reverse titrations (0·2 to 29·4 mg of hexacyanoferrate(III) in the cell) were performed, the titrant being added from a micro-burette. Nitrogen was passed to stir the solutions, and the current was recorded after elapse of about 2 min. Suitable quantities of metal ions were added for the investigation of interferences.

TABLE I.—AMPEROMETRIC TITRATIONS IN ABSENCE OF METAL IONS IN AMMONIUM CITRATE AND GLYCINE BUFFERS

Cobalt(II) taken, *mg/l*	Direct titrations cobalt(II) found, *mg/l*		Reverse titrations cobalt(II) found, *mg/l*	
	−0·3 V	−1·55 V	−0·3 V	−1·55 V
	Ammonium citrate solution			
29·5	29·5	—	29·5	—
5·89	5·89	—	5·83	—
2·95	2·92	2·98	2·92	2·95
0·29		0·30	0·29	0·29
	Glycine solution			
29·7	—	—	29·65	—
2·97	—	—	2·97	—
0·29	—	—	0·29	—

TABLE II.—AMPEROMETRIC TITRATIONS OF COBALT(II) (29·5 mg/l) IN THE PRESENCE OF INTERFERING IONS IN AMMONIUM CITRATE AND GLYCINE BUFFER SOLUTIONS.

Foreign metal added, *mg/l*		Cobalt(II) found, *mg/l*	
		Direct titration	Reverse titration
	Ammonium citrate solution at −0·3 V		
Cu(II)	40	29·5	29·5
	160	—	28·9
Ni(II)	2900	29·5	29·5
Cr(III)	25	29·5	—
V(V)	20	29·5	29·5
	200	30·0	29·8
	Glycine solution at −0·55 V		
Mn(II)	27	—	29·5
	270	—	29·2
Fe(III)	280	—	29·5
Ni(II)	290	—	29·5
	2900	—	29·8
Ce(III)	30	—	29·5
	70	—	30·0
Cr(III)	26	—	29·5
	260	—	30·1

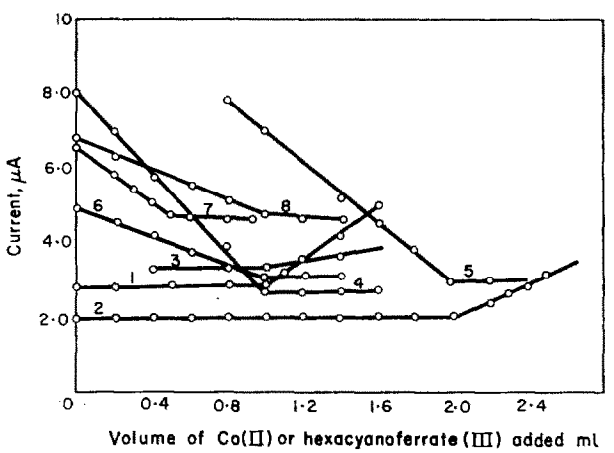

FIG. 1.—Amperometric titration curves at −0·3 V in ammonium citrate buffer at pH 9·8.
Direct titration of Co: *1*—$5 \times 10^{-4}M$; *2*—$10^{-3}M$; *3*—$5 \times 10^{-5}M$.
Reverse titration (Co as titrant): *4*—$5 \times 10^{-4}M$ Fe and Co; *5*—$10^{-3}M$ Fe and Co; *6*—$10^{-4}M$ Fe, $10^{-3}M$ Co; *7*—$5 \times 10^{-5}M$ Fe and Co; *8*—$2{\cdot}5 \times 10^{-5}M$ Fe, $5 \times 10^{-5}M$ Co (Fe = $[Fe(CN)_6]^{3-}$).

RESULTS AND DISCUSSION

The results of amperometric titrations are given in Tables I and II. Typical curves are shown in Fig. 1. From Table I it is evident that these titrations may be carried out successfully with fairly dilute solutions of cobalt(II). Errors of 1·0–1·8% were observed when $10^{-3}M$ solutions were titrated. In the ammonium citrate medium titrations could be carried out at potentials corresponding to the plateaux of cobalt(II) and hexacyanoferrate(III) but in the glycine buffer they were successful only at a potential on the hexacyanoferrate(III) wave (−0·55 V). Separate experiments showed that the binuclear complex formed in the glycine medium was reduced in the vicinity of the other potential (−1·50 V). This might be one of the reasons for the failure of the titrations at −1·5 V in this medium.

In ammonium citrate no interference was observed from copper(II), nickel(II), chromium(III) and vanadium(V), except that reverse titrations could not be successfully carried out in presence of chromium(III). This might be attributed to the oxidation of chromium(III) to chromate. Nickel(II) and vanadium(V) in up to 100-fold amounts did not interfere in the reverse titrations. Determinations were not possible in presence of cerium(III) and iron(III), owing to oxidation to cerium(IV) and precipitation of hydrous iron(III) oxide respectively.

In glycine medium both copper(II) and vanadium(V) interfered even when present in traces, and cerium(III) and chromium(III) when present in more than 10-fold amounts.

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Summary—An amperometric titration of cobalt(II) with hexacyanoferrate(III) in aqueous ammonium citrate or aqueous glycine solution at pH 9·8 or pH 8·0 respectively, is reported. Cobalt concentrations of 2–30 mg/l were successfully determined. In citrate solutions cerium(III) and iron(III) interfered, and in glycine solutions, copper(II) and vanadium(V).

Zusammenfassung—Es wird über eine amperometrische Titration von Kobalt(II) mit Hexacyanoferrat(III) in wäßriger Ammoncitrat- oder Glycinlösung bei pH 9,8 bzw. 8,0 berichtet. Kobaltkonzentrationen von 2–30 mg/l wurden mit Erfogl bestimmt. In Citratlösungen störten Cer(III) und Eisen(III), in Glycinlösungen Kupfer(II) und Vanadium(V).

Résumé—On décrit un titrage ampérométrique du cobalt(II) au moyen d'hexacyanoferrate(III) en citrate d'ammonium aqueux ou en solution aqueuse de glycine à pH 9,8 ou pH 8,0 respectivement. On a dosé avec succès des concentrations en cobalt de 2–30 mg/l. En solutions de citrate, le cérium(III) et le fer(III) gênent; le cuivre(II) et le vanadium(V) interfèrent en solutions de glycine.

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Selective spot test for hydrazine*

(*Received* 31 *March* 1967. *Accepted* 24 *May* 1967)

KUL'BERG and Cherkesov[1] described a sensitive assay and spot test for hydrazine based on its reaction with picryl chloride to form intensely violet hexanitrohydrazobenzene. However, this assay is not readily applicable to aqueous solutions of hydrazine, since the picryl chloride precipitates from solution and is partly hydrolysed to picric acid.[2]

We have found that trinitrobenzene sulphonic acid (TNBS), a stable water-soluble reagent, reacts with hydrazine to form violet hexanitrohydrazobenzene in weakly alkaline solutions. Monosubstituted hydrazines and primary amines combine with TNBS to form yellow, orange or pink *N*-picryl derivatives. *N,N'*-disubstituted hydrazines do not react. Typical reactons are shown in Fig. 1.

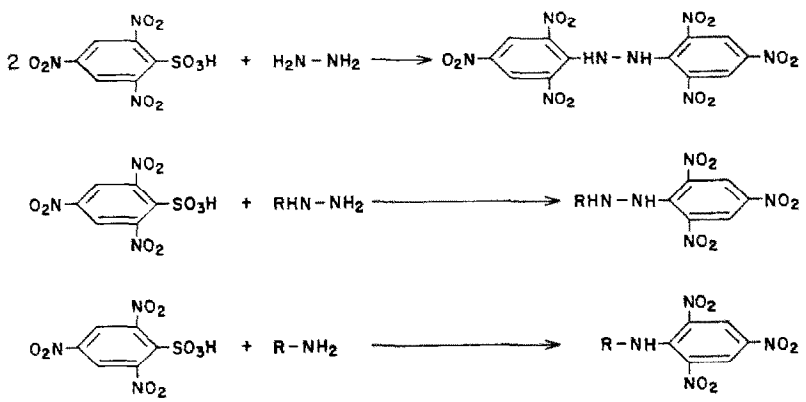

FIG. 1

Serial dilutions of hydrazine and its derivatives were tested with alkaline TNBS. At high concentrations, most gave a dark cherry red colour. Table I lists the identification limits and the colour at the identification limit. The violet colour from hydrazine was unmistakably different from the colour obtained from the hydrazine derivatives. Moreover the violet colour was readily observed when the test was conducted on samples containing equimolar amounts of hydrazine and methylhydrazine, propylhydrazine or phenylhydrazine.

N,N'-dimethylhydrazine, *N,N'*-dicarbethoxyhydrazine, *N,N'*-diacetylhydrazine, 1-acetyl-2-phenyl hydrazine, isonicotinylhydrazone of pyruvic acid, phthalic hydrazide, maleic hydrazide, citraconic hydrazide and luminol did not react with TNBS under the conditions described.

Reagents

Trinitrobenzene sulphonic acid reagent: 0·2% solution in water.
Sodium carbonate, 0·2*M*.

Procedure

To one drop of the test solution in a micro test-tube or on a spot-plate add one drop of trinitrobenzene sulphonic acid reagent and one drop of sodium carbonate solution. A violet colour appearing within 2 min is a positive test for hydrazine. If the colour is a dark red, dilute the test solution 10-fold and repeat the procedure.

Limit of identification 0·02 μg of hydrazine
Concentration limit $1:2{\cdot}5 \times 10^6$

* Issued as N.R.C. No. 9756.

TABLE I.—COMPOUNDS REACTING WITH TRINITROBENZENE SULPHONIC ACID

Compound	Colour	Limit of identification, μg
Hydrazine	Violet	0·02
Methylhydrazine	Orange	0·2
2-Hydroxyethylhydrazine	Orange	0·5
Propylhydrazine	Pink-orange	0·5
Isopropylhydrazine	Pink-orange	0·5
Phenylhydrazine	Pink-orange	1
p-Carboxyphenylhydrazine	Orange	1
2,4-Dinitrophenylhydrazine	Orange	4
Naphthylhydrazine	Yellow-brown	4
Aminoguanidine	Pink-orange	1
Triaminoguanidine	Brown-red	1
Carbohydrazide	Pink-brown	0·5
Butyric hydrazide	Pink	0·5
β-Hydroxybutyric hydrazide	Pink-orange	0·5
Lactic hydrazide	Orange-brown	1
Capric hydrazide	Orange	1
Aspartic acid β-hydrazide	Yellow	0·5
Glutamic acid γ-hydrazide	Yellow-orange	1·0
Oxalic dihydrazide	Orange	0·5
Malonic dihydrazide	Pink	1
Succinic dihydrazide	Pink	0·5
Glutaric dihydrazide	Pink	1
Adipic dihydrazide	Orange	0·5
Pimelic dihydrazide	Orange	0·5
Suberic dihydrazide	Orange	0·5
Cyclopropane carboxylic hydrazide	Pink	0·5
Benzoic hydrazide	Orange	0·5
Salicyclic hydrazide	Orange-brown	0·5
m-Nitrobenzoic hydrazide	Orange	0·2
p-Nitrobenzoic hydrazide	Orange-brown	0·1
p-Aminobenzoic hydrazide	Orange	1
4-Toluic hydrazide	Orange	1
Syringic hydrazide	Orange-pink	0·5
3,4,5-Trimethoxybenzoic hydrazide	Yellow	0·5
Benzilic hydrazide	Yellow	2
Mandelic hydrazide	Orange-pink	2
Phenylacetic hydrazide	Orange-pink	2
Indole-3-acetic hydrazide	Orange-pink	1
Indole-3-propionic hydrazide	Orange	1
Isonicotinic hydrazide	Orange	0·5
Ammonium chloride	Yellow	4
Hydroxylamine	Red-orange	2
DL-Alanine	Yellow	2
Albumin	Yellow	30
Aniline	Yellow	2

The concentration limit is dependent on the method of dilution. Aqueous solutions of hydrazine are unstable and dilutions should be made carefully in clean acid-rinsed glass-ware in a stepwise manner.

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Summary—Trinitrobenzene sulphonic acid reacts with hydrazine in dilute aqueous solution to give a violet colour. This reaction is used as the basis of a sensitive spot test for hydrazine.

Résumé—L'acide trinitrobenzène sulfonique réagit avec l'hydrazine en solution aqueuse diluée pour donner une coloration violette. Cette réaction est utilisée comme base d'un essai à la touche sensible pour l'hydrazine.

Zusammenfassung—Trinitrobenzolsulfonsäure reagiert in verdünnter wäßriger Lösung mit Hydrazin und gibt eine violette Färbung. Diese Reaktion wird zu einer empfindlichen Tüpfelprobe auf Hydrazin ausgenutzt.

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Determination of micro-amounts of beryllium in urine

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A NUMBER of methods have been reported for the determination of microgram amounts of beryllium in urine.[1–8] A combination of steps such as precipitation with inorganic carrier, ion-exchange separation, solvent extraction and mercury cathode electrolysis is involved in these methods for the concentration and separation of beryllium prior to its determination. In continuation of our earlier studies,[9] we have used organic co-precipitants for the concentration and separation of beryllium from urine. The co-precipitation of beryllium with Methylene Blue and tannin is carried out directly on the urine sample, and there is no need to destroy the organic matter present in the urine or to remove the inorganic constituents.

EXPERIMENTAL

Reagents

Standard beryllium solution containing 5·0 μg/ml was prepared as recommended by Sandell.[10] Working solutions containing 1·0, 0·2 and 0·02 μg of beryllium per ml were prepared by suitable dilutions of the standard.

Stock Morin solution, 0·05% w/v in ethyl alcohol, was diluted 10-fold with distilled water for use.

Triethanolamine solution 3% v/v in water.

Tetrasodium ethylenediaminetetra-acetate solution (Na_4Y). A suspension of 25 g of disodium EDTA was dissolved by the slow addition of 134 ml of 1·0*M* sodium hydroxide and diluted to 500 ml with distilled water.

Quinine sulphate reference solution (1×10^{-4}% in 0·1*N* sulphuric acid) was prepared by proper dilution of a 0·1% solution in 0·1*N* sulphuric acid.

Methylene Blue solution, 1% w/v in water.

Tannin solution, 10% w/v in water.

Disodium EDTA solution (Na_2H_2Y), saturated.

Apparatus

Jarrell-Ash GM Fluorimeter Mark V with solution attachment.

Procedure for the fluorimetric determination of beryllium

The procedure followed for the determination of beryllium in the range 0·1–1·0 μg was the same as that given by Sandell,[10] except that the addition of stannite was not found necessary and that 1 ml of triethanolamine solution was added to complex heavy metals.

Summary—Trinitrobenzene sulphonic acid reacts with hydrazine in dilute aqueous solution to give a violet colour. This reaction is used as the basis of a sensitive spot test for hydrazine.

Résumé—L'acide trinitrobenzène sulfonique réagit avec l'hydrazine en solution aqueuse diluée pour donner une coloration violette. Cette réaction est utilisée comme base d'un essai à la touche sensible pour l'hydrazine.

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TABLE I.—RECOVERY OF BERYLLIUM FROM URINE

Sample volume, *ml*	Be taken, *μg*	Be recovered, *μg*
200	5·0, 5·0	4·7, 4·8
100	1·0	1·0
100	0·10	0·103 ± 0·009*
100	0·020	0·021 ± 0·004†
1000	Carrier-free ^{7}Be (4300 ± 65 cpm)	4224 ± 65 cpm

* Standard deviation (9 variates).
† Standard deviation (7 variates).

For the range 0·01–0·1 μg of beryllium, sample aliquots were taken in 10-ml Pyrex beakers, 2·5 ml of Na_4Y solution and 1 ml of triethanolamine solution were added to each of the beakers, and the pH of the solutions was adjusted to 11·6–11·9 with sodium hydroxide. The solutions were cooled in an ice-bath for 10 min. Then 0·2 ml of the working solution of Morin was added to each of them and mixed well. The solutions were transferred to 10-ml volumetric flasks and made up to volume with distilled water. The flasks were kept in the ice-bath for a further 10 min, and then 5-ml portions were transferred to clean fluorimetric tubes, the temperature was allowed to rise to 15 ± 1°, and the fluorescence was measured immediately.

Procedure for the co-precipitation of beryllium

To a suitable volume of urine sample (100–1000 ml), add 10 ml of Na_2H_2Y solution and adjust the pH to 8 with sodium hydroxide. Add a few drops of tannin solution followed by 20 ml of Methylene Blue solution and stir well. Add 7 ml more of tannin solution and stir again. Allow the precipitate to settle, filter it off on Whatman No. 540 paper and wash it several times with 0·5% ammonium chloride solution adjusted to pH 8. Dry the precipitate under an infrared lamp, and ignite it in a platinum crucible at 500°. Treat the residue with a drop or two of hydrofluoric acid and 2 ml of perchloric acid and heat almost to dryness on a sand-bath. Add small portions of 5% v/v hydrochloric acid and transfer the solution to a volumetric flask and make up to the mark. Take suitable aliquots of this solution for the fluorimetric determination already described. If the amount of beryllium is less than 0·1 μg use all the residue solution for the fluorimetric determination. Recoveries from urine to which known amounts of beryllium had been added are given in Table I.

Co-precipitation of other ions

A number of cations were studied for their co-precipitation behaviour under the conditions used for beryllium in pure solution.[9] The results are given in Table II.

RESULTS AND DISCUSSION

In the fluorimetric procedure given above for the determination of beryllium in the range 0·1–1·0 μg, it was found that the fluorescence was stable for more than 3 hr if the solutions were not continuously exposed to ultraviolet light. This is in agreement with Sill's findings.[11] In the lower range of 0·01–0·1 μg of beryllium, though the fluorescence was stable in pure solutions it faded rapidly in sample solutions. However, the fluorescence could be stabilized for up to 8 hr by keeping the solutions below 15°. Moreover, it was observed that the sensitivity was then about 25% greater than for measurements made at room temperature. Laitinen[5] has reported a similar increase in the intensity of beryllium–Morin fluorescence at low temperatures.

It can be seen from Table II that though a number of cations accompany beryllium, the co-precipitation of alkali and alkaline earth metals is poor. The precipitation of calcium phosphate in the urine sample at the pH used is prevented by adding EDTA. Thus it is possible by this method to collect beryllium in a single step free from any of the major inorganic constituents present in urine. No prior treatment of the sample is required either to destroy the organic matter or to remove the inorganic constituents present in it. The only other step required before the fluorimetric determination of beryllium is simple ignition of the organic matrix (the precipitate of tannin and Methylene Blue).

The results in Table I show that the reagents used in this method are efficient in collecting micro and sub-micro amounts of beryllium from urine samples. The relative standard deviations at concentrations of beryllium of 0·1 and 0·02 μg/100 ml of urine sample were 9% and 19% respectively.

TABLE II.—BEHAVIOUR OF OTHER CATIONS IN THE PRECIPITATION OF METHYLENE BLUE AND TANNIN

Ion	Amount taken μg	Recovery %
Sm(III)	10	100
La(III)	10	103
Y(III)	10	93
Zn(II)	10	100
Co(II)	10	95
Th(IV)	10	100
Sc(III)	10	100
Pb(II)	10	91
Hf(IV)	10	102
W(VI)	100	94
Ga(III)	10	87
As(III)	10	29
Se(IV)	10	0
Tl(I)	10	25
Ca(II)	100	6
Sr(II)	100	2
Sn(II)	100	1
Fe(III)	50	100
Cr(VI)	50	100
Ni(II)	50	100
Mo(VI)	50	90
Mn(II)	50	100
Cu(II)	50	100
U(VI)	10	100
Na(I)	100	2
K(I)	100	2
Li(I)	100	0
Mg(II)	100	15

Elements from Sm(III) to Sn(II) were assayed radiometrically by use of suitable tracers; Fe(III) to Cu(II) spectrophotometrically; U fluorimetrically; Na, K and Li by flame photometry; Mg by EDTA titration.

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Summary—Methylene Blue and tannin are used to collect beryllium from urine by co-precipitation. After ignition the beryllium is brought into solution and determined fluorimetrically with Morin. When the amount of beryllium is less than 0·1 μg, measurements are carried out at low temperature to prevent fading of the fluorescence. In this method beryllium is collected and separated in a single step and no prior treatment of the urine sample is required either to destroy the organic matter or to remove the inorganic constituents present in it. The relative standard deviations for the determination of 0·1 and 0·02 μg of Be/100 ml of urine sample were 9 and 19% respectively.

Zusammenfassung—Zur Anreicherung von Beryllium aus Urin durch Mitfällung werden Methylenblau und Tannin verwendet. Nach Verglühen wird das Beryllium in Lösung gebracht und fluorimetrisch mit Morin bestimmt. Bei kleineren Berylliummengen als 0,1 μg werden

die Messungen bei tiefer Temperature ausgeführt, um Nachlassen der Fluoreszenz zu vermeiden. Bei dieser Vorschrift wird Beryllium in einem einzigen Arbeitsgang gesammelt und abgetrennt, ohne daß der Urin zur Zerstörung des organischen Materials oder der anorganischen Bestandteile einer Vorbehandlung bedürfte. Die relativen Standardabweichungen bei der Bestimmung von 0,1 und 0,02 μg Beryllium in 100 ml Urinprobe waren 9 und 19%.

Résumé—On utilise le bleu de méthylène et le tannin pour recueillir le béryllium de l'urine par coprécipitation. Après calcination, le béryllium est mis en solution et dosé par fluorimétrie au morin. Lorsque la quantité de béryllium est inférieure à 0,1 μg, les mesures sont menées à basse température pour éviter l'affaiblissement de la fluorescence. Dans cette méthode, le béryllium est recueilli et séparé en un seul stade et aucun traitement préalable de l'urine n'est necessité, soit pour détruire la matière organique, soit pour éliminer les constituants inorganiques qu'elle renferme. Les écarts types relatifs pour le dosage de 0,1 et 0,02 μg de Be/100 ml d'échantillon d'urine sont de 9 et 19% respectivement.

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Homogeneous precipitation of basic aluminium benzoate with a buffer solution

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It has been shown that homogeneous precipitation by addition of a buffer solution of pH just sufficient to precipitate the required hydroxide produces an easily filterable precipitate and is more easily controlled than by the urea hydrolysis method.

Britton[2] gives the following values for the pH at which metal sulphates just start to precipitate as hydroxides; iron(III), 2: aluminium, 4·1: chromium(III), 5·3: copper(II), 5·3: iron(II), 5·5; beryllium, 5·7: nickel, 6·7: cadmium, 6·7: cobalt(II), 6·8: zinc, 7·0: manganese(II), 8·6: magnesium, 10·5.

Replacing sulphate by benzoate should not change this order but separate experiments have shown that aluminium solutions first appear cloudy at pH 3·1 in the presence of benzoic acid and one might expect a comparable lowering for other metal hydroxides. The basic aluminium benzoate is completely precipitated at pH 3·7, just below the pH of maximum buffer capacity of the benzoic acid benzoate system (pK, 4·2). The quantitative precipitation of aluminium can be achieved in the presence of a large excess of cadmium, calcium, cobalt, copper, manganese, nickel and zinc.

die Messungen bei tiefer Temperature ausgeführt, um Nachlassen der Fluoreszenz zu vermeiden. Bei dieser Vorschrift wird Beryllium in einem einzigen Arbeitsgang gesammelt und abgetrennt, ohne daß der Urin zur Zerstörung des organischen Materials oder der anorganischen Bestandteile einer Vorbehandlung bedürfte. Die relativen Standardabweichungen bei der Bestimmung von 0,1 und 0,02 μg Beryllium in 100 ml Urinprobe waren 9 und 19%.

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Homogeneous precipitation of basic aluminium benzoate with a buffer solution

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It has been shown that homogeneous precipitation by addition of a buffer solution of pH just sufficient to precipitate the required hydroxide produces an easily filterable precipitate and is more easily controlled than by the urea hydrolysis method.

Britton[2] gives the following values for the pH at which metal sulphates just start to precipitate as hydroxides; iron(III), 2: aluminium, 4·1: chromium(III), 5·3: copper(II), 5·3: iron(II), 5·5; beryllium, 5·7: nickel, 6·7: cadmium, 6·7: cobalt(II), 6·8: zinc, 7·0: manganese(II), 8·6: magnesium, 10·5.

Replacing sulphate by benzoate should not change this order but separate experiments have shown that aluminium solutions first appear cloudy at pH 3·1 in the presence of benzoic acid and one might expect a comparable lowering for other metal hydroxides. The basic aluminium benzoate is completely precipitated at pH 3·7, just below the pH of maximum buffer capacity of the benzoic acid benzoate system (pK, 4·2). The quantitative precipitation of aluminium can be achieved in the presence of a large excess of cadmium, calcium, cobalt, copper, manganese, nickel and zinc.

EXPERIMENTAL

Reagents

Buffer, pH 4·25–4·35. Dissolve 45 g of ammonium chloride, 5 g of benzoic acid and 15 g of ammonium benzoate in 2 l. of water.

Ammonium benzoate. Add excess of ammonia to a solution of recrystallized benzoic acid. Concentrate the solution to incipient crystallization, making sure that ammonia is present in slight excess, then cool rapidly, and dry at 90° the crystals which separate.

Standard aluminium solution, 1 *g/l*. Dissolve about 1 g of pure aluminium (accurately weighed) in dilute hydrochloric acid and dilute to 1 l.

Stock solutions of other metals were prepared by dissolving the appropriate amounts of the chlorides in water. These solutions were not standardized.

Procedure

To 350 ml of the benzoate buffer add 50 ml of standard aluminium solution which has been treated first with enough aqueous ammonia to give a faint permanent cloudiness and then by careful addition of dilute hydrochloric acid until the solution is clear.

Boil the solution for 2 min, allow it to stand for 30 min and filter off the precipitate on a retentive paper. The pH of the filtrate is typically 3·98, well above the pH at which all the aluminium is precipitated.

Wash the precipitate with 2% ammonium benzoate solution adjusted to pH 4·2 (Bromocresol Green indicator) and ignite to Al_2O_3 at 1250°.

RESULTS AND DISCUSSION

Typical results for 0·0854 g of Al_2O_3 taken are 0·0853, 0·0855, 0·0852 g by the ammonia method[a] and 0·0854, 0·0853, 0·0854 g by the proposed method.

Filtration is rapid and the determination can be carried out very much faster than by the standard ammonia method. Washing the precipitate with 1% ammonium chloride led to low results, owing to dissolution of the precipitate, even though the pH of the wash solution had been adjusted to pH 4·2; it had dropped to 3·2 by the end of the washing. Ammonium benzoate wash solution adjusted to pH 4·2 did not change in pH on passing through the filter.

The procedure was used to determine aluminium in the presence of other metal ions, and the results are given in Table I.

TABLE I.—DETERMINATION OF ALUMINIUM IN THE PRESENCE OF OTHER METAL IONS

Al_2O_3 taken, *g*	Other metal ion present, *g*	Al_2O_3 found, *g*
0·0853	0·24 Mn	0·0854
	0·36 Mn	0·0855
0·0853	0·41 Ca	0·0854
	0·67 Ca	0·0853
0·0853	0·18 Cd	0·0852
	0·25 Cd	0·0852
0·0853	0·42 Ni	0·0856
	0·52 Ni	0·0855
0·0855	0·40 Co	0·0856
	0·50 Co	0·0855
0·0855	0·31 Cu*	0·0854
0·0855	0·75 Cu*	0·0853
0·0853	0·21 Zn	0·0852†
0·0853	0·45 Zn	0·0853‡

* Reduced to copper(I) with $NH_2OH.HCl$ before the precipitation.

† Reprecipitation: 0·8 mg of Zn accompanied the aluminium in the first precipitation.

‡ Reprecipitation: 1·7 mg of Zn accompanied the aluminium in the first precipitation.

These results show that aluminium can be satisfactorily determined in the presence of a large excess of manganese, calcium, cadmium, nickel and cobalt without any complications. In the case of copper it was found that a small amount of copper(II) benzoate precipitated with the aluminium hydroxide, but this interference could be satisfactorily overcome by previous reduction to copper(I) with hydroxylamine hydrochloride or by double precipitation without the reduction. Similarly with zinc there is appreciable coprecipitation which can be overcome by a second precipitation.

Chromium, iron and beryllium all caused difficulties which necessitates a preliminary separation of these elements. Reduction of iron to iron(II) did not prove to be feasible as it was impossible to prevent aerial oxidation at the surface of the liquid. Chromium and beryllium both coprecipitated extensively with aluminium at pH 4 even though one would not expect their hydroxides to form at pH values below 5·3 and 5·7 respectively.

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Summary—Addition of an ammonium benzoate–benzoic acid buffer solution to a solution of aluminium ions gives a homogeneous precipitation of basic aluminium benzoate. This has advantages over the urea method for the gravimetric determination of aluminium in the presence of large quantities of manganese, calcium, cadmium, nickel, cobalt, copper, and zinc ions.

Zusammenfassung—Die Zugabe einer Ammoniumbenzoat–Benzoesäure-Pufferlösung zu einer Lösung von Aluminiumionen ergibt eine homogene Fällung von basischem Aluminiumbenzoat. Dieses Verfahren hat bei der gravimetrischen Bestimmung von Aluminium in Gegenwart großer Mengen Mangan, Calcium, Cadmium, Nickel, Kobalt, Kupfer und Zink Vorteile vor der Harnstoffmethode.

Résumé—L'addition d'une solution tampon benzoate d'ammonium-acide benzoïque à une solution d'ions aluminium donne lieu à une précipitation homogène de benzoate basique d'aluminium. Ceci offre des avantages par rapport à la méthode à l'urée pour le dosage gravimétrique de l'aluminium en présence de fortes quantités d'ions manganèse, calcium, cadmium, nickel, cobalt, cuivre et zinc.

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Studies on metallochromic indicators—II

Zincon and its mercury and zinc complexes as indicators in EDTA titrations

(*Received* 8 *May* 1967. *Accepted* 30 *June* 1967)

ZINCON (2-carboxy-2′-hydroxy-5′-sulphoformazylbenzene), a well known colorimetric reagent for copper, zinc and mercury,[1–3] was introduced in chelometry for the direct EDTA titration of zinc and the indirect titrations of copper(II), nickel, cobalt(II), iron(III), manganese(II), cadmium, lead, cerium(III), indium, calcium, chromium and aluminium *via* back-titration of excess of EDTA with a

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Chromium, iron and beryllium all caused difficulties which necessitates a preliminary separation of these elements. Reduction of iron to iron(II) did not prove to be feasible as it was impossible to prevent aerial oxidation at the surface of the liquid. Chromium and beryllium both coprecipitated extensively with aluminium at pH 4 even though one would not expect their hydroxides to form at pH values below 5·3 and 5·7 respectively.

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Résumé—L'addition d'une solution tampon benzoate d'ammonium-acide benzoïque à une solution d'ions aluminium donne lieu à une précipitation homogène de benzoate basique d'aluminium. Ceci offre des avantages par rapport à la méthode à l'urée pour le dosage gravimétrique de l'aluminium en présence de fortes quantités d'ions manganèse, calcium, cadmium, nickel, cobalt, cuivre et zinc.

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standard solution of zinc in alkaline medium by Kinnunen and Merikanto.[4] Ringbom[5] and Reilley[6] have used the Zn–Zincon complex as indicator for the direct titration of calcium with EGTA in presence of magnesium. In the present investigation it has been observed that Zincon is a very suitable indicator for the direct titration of mercury(II) in slightly acidic medium (pH 5·5–7). In this pH range the Hg(II)–Zincon complex also acts as a suitable indicator for the direct titration of lead and cadmium. It has been further observed that lead and cadmium can be directly titrated with EDTA, the indicator being the Zn–Zincon complex in ammoniacal buffer (pH 9·5). Reilley[6] mentioned that in the EGTA titration of calcium by this method, use of too high a concentration (0·1*M*) of ammonia in the buffer causes competition between the various zinc-complexing agents and leads to unsharp end-points. This disadvantage is obviated in our method, where the titration is carried out with EDTA instead of EGTA, because the Zn–EDTA complex has a higher stability constant ($\log K = 16{\cdot}5$) than that of the Zn–EGTA complex ($\log K = 13{\cdot}0$). However, EDTA could not be used for the titration of calcium in the presence of magnesium, with which EDTA reacted completely, whereas EGTA did not.

The stability and colour intensity of the Hg–Zincon complex is maximum at pH 7, but the indicator can be used for titration of mercury(II) with EDTA at pH 5·5–7 in acetate buffer, there being a sharp colour change from blue to pale red at the end-point. The titration can be carried out even in the presence of equivalent concentrations of chloride and bromide. The method gave accurate results, error not exceeding 0·3%, when mercury(II) solutions, concentration 10–40 mg/50 ml, were titrated.

The titrations of lead and cadmium with EDTA, using Hg–Zincon complex as indicator in acetate buffer (pH 5·5–7) or Zn–Zincon indicator in ammoniacal buffer (pH 9·5) were found to have an experimental error of 0·3%. The titration with Hg–Zincon complex has the advantage that alkaline earths do not interfere.

EXPERIMENTAL

Reagents

Standard EDTA solution, 0·1*M*. Prepared from analytical reagent grade disodium salt.

Mercury(II), 0·1*M*. Prepared from analytical grade mercury(II) chloride and standardized.[7–8]

Standard lead, calcium and cadmium solutions, 0·1*M*. Prepared from the analytical grade nitrates and standardized by EDTA titration.

Solutions of other metal ions. Prepared from analytical grade salts.

All these solutions were prepared in conductivity water and were diluted to the desired molarities.

Zincon indicator solution. Prepared by dissolving 0·13 g of Zincon indicator (Light-Koch) in 2 ml of 1*M* sodium hydroxide and diluting to 100 ml.

Mercury(II)–EDTA complex solution. Prepared by mixing equal volumes of 0·1*M* EDTA and 0·1*M* mercury(II) solutions.

Zinc–EDTA complex solutions. Prepared by mixing equal volumes of 0·1*M* EDTA and 0·1*M* zinc solutions.

Buffer solutions. Buffer solutions of pH ranging from 4·5 to 7·0 were prepared by mixing appropriate volumes of 0·2*M* sodium acetate and 0·2*M* acetic acid, and of pH 9·5 and 10 by mixing appropriate volumes of 1*M* ammonium chloride and 1*M* ammonia. Final pH of the buffer solutions was checked with pH meter and adjusted.

Direct titration of Hg(II) with EDTA, with Zincon as indicator

Mercury(II) solution (50 ml containing 10 mg of mercury) was mixed with an equal volume of acetate buffer, pH 6, and 5–6 drops of Zincon indicator solution. The pH of the solution was adjusted to 6 with 0·2*M* sodium acetate, and checked with pH meter. The blue solution was titrated with 0·02*M* EDTA until the colour changed abruptly to pale red at the equivalence point. The titration was carried out with constant shaking. The colour change at the end-point was very sharp and reversible. In this titration Cu^{2+}, Ni^{2+}, Co^{2+}, VO^{2+}, Fe^{3+}, Ga^{3+}, In^{3+}, Tl^{3+}, Al^{3+}, La^{3+} and Sm^{3+} caused interference even when present in traces, by blocking the indicator. Pb^{2+}, Cd^{2+}, Zn^{2+} and Mn^{2+} were co-titrated and when present in appreciable amounts gave a titration value which corresponded to the sum of the metal ions, except for Zn^{2+} and Mn^{2+} where it was always found to be less. Mercury could be accurately titrated even in the presence of tenfold amounts of alkaline earths. Chloride and bromide did not interfere when present in up to equivalent proportions but only traces of iodide could be tolerated. Other anions such as sulphate, acetate, nitrate did not interfere but phosphate, oxalate, citrate and tartrate did.

Direct titration of Pb^{2+} or Cd^{2+} with EDTA, with Hg(II)–Zincon as indicator

Ten ml of the metal ion solution (0·02*M*) were mixed with an equal volume of acetate buffer, pH 6, and 5–6 drops of the Zincon solution. When 1 ml of 0·1*M* Hg(II)–EDTA complex solution

was added to it a blue colour developed. The solution was titrated with 0·02*M* EDTA with constant shaking. At the equivalence point the colour changed to pale red. The colour change was sharp and reversible. In this titration Cu^{2+}, Ni^{2+}, Co^{2+}, VO^{2+}, Fe^{3+}, Ga^{3+}, In^{3+}, Tl^{3+}, Al^{3+}, La^{3+} and Sm^{3+} caused interference even when present in traces, by blocking the indicator. The alkaline earths did not interfere and traces of Zn^{2+} and Mn^{2+} could be tolerated.

Direct titration of Pb^{2+}, Cd^{2+} or Ca^{2+} ions with EDTA, using Zn–Zincon indication

The metal solution was mixed with an equal volume of ammoniacal buffer, pH 9·5 or 10 (about 0·1 g of solid sodium tartrate was also added to the lead solution), 3–4 drops of Zincon solution, and 1 ml of Zn–EDTA complex solution. The same titration procedure was used. In this titration Cu^{2+}, Ni^{2+}, Co^{2+}, VO^{2+}, Fe^{3+}, Ga^{3+}, In^{3+}, Tl^{3+}, Al^{3+}, La^{3+} and Sm^{3+}, even when present in traces, blocked the indicator. The alkaline earths, Zn^{2+} and Mn^{2+} were cotitrated.

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Summary—Zincon has been found to be an excellent indicator in the titration of mercury(II) with EDTA at pH 5·5–7. Moreover the mercury(II)–Zincon and zinc–Zincon systems have been found to be suitable indicators in the direct EDTA titrations of Pb^{2+}, Cd^{2+} and Ca^{2+}. Interference studies of a number of cations and anions have been made. Chloride and bromide can be tolerated in the titration of mercury(II), up to equivalent concentrations.

Résumé—On a trouvé que le Zincon est un excellent indicateur pour le dosage du mercure(II) à l'EDTA à pH 5,5–7. En outre, on a trouvé que les systèmes mercure (II)–Zincon et zinc–Zincon sont des indicateurs convenables pour les titrages directs à l'EDTA de Pb^{2+}, Cd^{2+} et Ca^{2+}. On a fait une étude sur les interférences d'un certain nombre de cations et d'anions. On peut tolérer le chlorure et le bromure dans le dosage du mercure(II) jusqu'à des concentrations équivalentes.

Zusammenfassung—Zincon ist ein ausgezeichneter Indikator bei der Titration von Quecksilber(II) mit EDTA bei pH 5,5–7. Darüber hinaus sind die Systeme Quecksilber(II)–Zincon und Zink–Zincon geeignete Indikatoren bei der direkten EDTA-Titration von Pb^{2+}, Cd^{2+} und Ca^{2+}. Die Störung von einer Anzahl Kat- und Anionen wurde untersucht. Chlorid und Bromid können bis zu äquimolaren Mengen bei der Titration von Quecksilber(II) anwesend sein.

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Successive chelatometric titration of calcium and magnesium

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3′,3″-BIS(2-HYDROXY-3-CARBOXY-NAPHTHALENEAZO)PHENOLPHTHALEIN (BNP)[1] can be used as a metallochromic indicator for the alkaline earths. At pH 10 the colour of the reagent is red-violet and that of the chelate is blue, whereas above pH 12 the colours are blue-violet and red respectively. Thus the reagent can be used as an indicator for the successive chelatometric titration of calcium and magnesium in natural waters, by a simple procedure; calcium is titrated at pH 13, the end-point colour change being from red to blue-violet, and then after adjustment of the pH to 10 the magnesium is titrated, with a colour change from blue to red-violet at the end-point.

This procedure is reliable and is simpler than that due to Patton and Reeder.[2]

EXPERIMENTAL

Reagents

EDTA solution, 0·01M. Standardized with standard 0·01*M* zinc solution prepared from zinc that is 99·999% pure.

Calcium solution, 0·01M. Dissolve calcium carbonate in hydrochloric acid, dilute to volume and standardize with EDTA.

Magnesium sulphate solution, 0·01M. Standardized with EDTA.

BNP, 0·1% aqueous solution. Prepare BNP by the published procedure[1] and dissolve it in a small amount of acetone before diluting with water.

Other reagents are of analytical grade.

Procedures

Determination of calcium. Add to 100 ml of calcium solution (~0·001*M*) 0·2–0·5 g of potassium hydroxide and a few drops of the indicator solution. Titrate with 0·01*M* EDTA till the colour turns from red to blue-violet. The colour change is improved by addition of 10 ml of acetone to the solution, but the acetone must be omitted if magnesium is to be titrated subsequently, as it makes that end-point indistinct.

Determination of magnesium. Magnesium is titrated by the same method as calcium but at pH 10. At the end-point the colour changes from blue to red-violet, but it is somewhat difficult to detect the end-point, because the colour change proceeds slowly.

Successive titration for calcium and magnesium. Add, to 50 ml of sample solution containing calcium and magnesium, a few drops of the indicator and 0·3 g of potassium hydroxide to adjust the pH to 13. Titrate with 0·01*M* EDTA till the colour changes from red to blue-violet.

Acidify with 0·3 ml of concentrated hydrochloric acid and dissolve the magnesium hydroxide precipitate completely. Add a few drops of 3*M* ammonia till the colour becomes blue. Add 5 ml of ammonia-ammonium chloride buffer solution (pH 10) and a few more drops of the indicator if the colour has faded.

Continue the titration till the colour turns from blue to red-violet.

RESULTS AND DISCUSSION

The colour of the indicator when free or complexed is greatly affected by pH (Table I). Results of typical titrations of calcium, magnesium and mixtures of the two ions are shown in Tables II, III and IV respectively. Iron(III) interferes but can be effectively masked with triethanolamine. If a large amount of magnesium is present there will be the usual risk of coprecipitation of calcium on the magnesium hydroxide precipitate.

TABLE I.—COLOURS OF BNP AND Ca- OR Mg-BNP AT VARIOUS pH VALUES

Reagent	red	purple				violet	blue-violet
pH	7·7 8·6	9·0 9·6	9·8 10·0 10·2	10·4	10·9	11·6	13·1
Complex	violet	blue-violet	blue	blue-violet	violet		red

TABLE II.—DETERMINATION OF CALCIUM

Acetone absent			10% Acetone present		
Ca^{2+} taken, *mg*	pH	Ca^{2+} found, *mg*	Ca^{2+} taken, *mg*	pH	Ca^{2+} found, *mg*
4·02	12·8	4·00	4·02	12·5	4·00
4·02	13·0	4·02	4·02	12·8	4·01
4·02	13·0	4·02	4·02	13·1	4·01
4·02	13·2	4·02	4·02	13·3	4·02
			4·02	13·5	4·02

TABLE III.—DETERMINATION OF MAGNESIUM

pH	Mg^{2+} taken, *mg*	Mg^{2+} found, *mg*
9·8	2·44	2·45
10·0	2·44	2·44
10·2	2·44	2·45

TABLE IV.—DETERMINATION OF CALCIUM AND MAGNESIUM

Ca^{2+}:Mg^{2+}	pH 13		pH 10	
	Ca^{2+} taken, *mg*	Ca^{2+} found, *mg*	Mg^{2+} taken, *mg*	Mg^{2+} found, *mg*
5:0·5	2·01	2·01	0·12	0·12
5:1	2·01	2·01	0·25	0·24
5:3	2·01	2·01	0·73	0·73
5:5	2·01	2·01	1·22	1·22
3:5	1·20	1·20	1·22	1·22
1:5	0·40	0·40	1·22	1·22
0·5:5	0·20	0·20	1·22	1·22

TABLE V.—DETERMINATION OF CALCIUM AND MAGNESIUM IN WATER

		0·01*M* EDTA, *ml*					
		Ca^{2+}			Mg^{2+}		
		BNP	NN*	diff.	BNP	EBT†	diff.
River water	A	1·39	1·39	±0·00	0·59	0·61	−0·02
	B	1·92	1·92	±0·00	0·70	0·70	±0·00
	C	2·08	2·08	±0·00	0·76	0·77	−0·01
Underground water	D	4·31	4·31	±0·00	2·73	2·75	−0·02
	E	6·03	6·04	−0·01	4·14	4·11	+0·03
	F	9·72	9·72	±0·00	2·50	2·48	+0·02

* Patton–Reeder indicator.[2]
† Eriochrome Black T.

Calcium and magnesium in river water and underground water have been determined by this method, and the results compared with the ordinary method in which the indicators were Patton and Reeder's for calcium, and Eriochrome Black T for magnesium (Table V).

This method was more convenient and faster than the ordinary chelatometric method for calcium and magnesium in water.

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Summary—A simple procedure for the successive chelatometric titration of calcium and magnesium in natural waters, with 3′,3″-bis(2-hydroxy-3-carboxy-naphthaleneazo)phenolphthalein as indicator, is described.

Zusamnenfassung—Eine einfache Vorschrift zur chelometrischen Titration von Calcium und Magnesium in Naturwässern nacheinander wird beschrieben. Sie arbeitet mit 3′,3″-Bis(2-hydroxy-3-carboxy-naphthalinazo)phenolphthalein als Indikator.

Résumé—On décrit une technique simple pour les titrages chélatométriques successifs du calcium et du magnésium dans les eaux naturelles avec la 3′,3″-bis (2-hydroxy-3-carboxynaphtalèneazo) phénolphtaléine comme indicateur.

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Controlled potential coulometric determination of uranium and neptunium in uranium–neptunium alloys*

THE need for an analytical method for the determination of uranium and neptunium in the presence of each other arose when our Metallurgical Laboratory prepared a uranium-neptunium alloy. It appeared obvious that these two elements could not be determined by the normal analytical procedures if the necessary precision and accuracy were to be attained. Controlled potential coulometry, however, seemed to offer the necessary precision, accuracy, and freedom from interference. It would also eliminate the necessity of a separation of these elements before an analysis could be performed.

The controlled potential coulometric determination of uranium has been widely investigated, as can be seen from the numerous papers on the subject.[1–4] Stromatt[5] has reported the successful controlled potential coulometric determination of neptunium. There is, however, no report of these elements being determined in the presence of each other.

EXPERIMENTAL

Apparatus

A Numec Model 6000 controlled potential coulometric titrator, described by Jones *et al.*,[6,7] and manufactured by Nuclear Materials and Equipment Corporation of Apollo, Pennsylvania, was used for this investigation. The titration cell and assembly have been described.[5]

* Work Performed Under U.S. Atomic Energy Commission Contract AT(29-1)-1106.

Calcium and magnesium in river water and underground water have been determined by this method, and the results compared with the ordinary method in which the indicators were Patton and Reeder's for calcium, and Eriochrome Black T for magnesium (Table V).

This method was more convenient and faster than the ordinary chelatometric method for calcium and magnesium in water.

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Summary—A simple procedure for the successive chelatometric titration of calcium and magnesium in natural waters, with 3′,3″-bis(2-hydroxy-3-carboxy-naphthaleneazo)phenolphthalein as indicator, is described.

Zusamnenfassung—Eine einfache Vorschrift zur chelometrischen Titration von Calcium und Magnesium in Naturwässern nacheinander wird beschrieben. Sie arbeitet mit 3′,3″-Bis(2-hydroxy-3-carboxy-naphthalinazo)phenolphthalein als Indikator.

Résumé—On décrit une technique simple pour les titrages chélatométriques successifs du calcium et du magnésium dans les eaux naturelles avec la 3′,3″-bis (2-hydroxy-3-carboxynaphtalèneazo) phénolphtaléine comme indicateur.

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Controlled potential coulometric determination of uranium and neptunium in uranium–neptunium alloys*

THE need for an analytical method for the determination of uranium and neptunium in the presence of each other arose when our Metallurgical Laboratory prepared a uranium-neptunium alloy. It appeared obvious that these two elements could not be determined by the normal analytical procedures if the necessary precision and accuracy were to be attained. Controlled potential coulometry, however, seemed to offer the necessary precision, accuracy, and freedom from interference. It would also eliminate the necessity of a separation of these elements before an analysis could be performed.

The controlled potential coulometric determination of uranium has been widely investigated, as can be seen from the numerous papers on the subject.[1–4] Stromatt[5] has reported the successful controlled potential coulometric determination of neptunium. There is, however, no report of these elements being determined in the presence of each other.

EXPERIMENTAL

Apparatus

A Numec Model 6000 controlled potential coulometric titrator, described by Jones *et al.*,[6,7] and manufactured by Nuclear Materials and Equipment Corporation of Apollo, Pennsylvania, was used for this investigation. The titration cell and assembly have been described.[5]

* Work Performed Under U.S. Atomic Energy Commission Contract AT(29-1)-1106.

Reagents

Stock solutions of uranium were prepared from standard sample 950a, U_3O_8, obtained from the U.S. National Bureau of Standards. Neptunium stock solutions were prepared by dissolving neptunium dioxide, 99·74% NpO_2, in concentrated nitric acid with heating. All other chemicals were reagent grade.

Neptunium procedure

A cell with a platinum gauze working electrode was used. A 15-ml volume of 0·5*M* sulphuric acid supporting electrolyte solution was placed in this titration cell and deaerated for 3 min with a stream of argon. The solution was prereduced at 0·66 V *vs.* the saturated calomel electrode (SCE) under an argon blanket until the cell current had decreased to 30 μA, and was then preoxidized at 1·02 V *vs.* SCE until the cell current had again decreased to 30 μA. An aliquot, containing from 0·5 to 5·0 mg of neptunium, was transferred to the titration cell, followed by 0·25 ml of 0·05*M* cerium(IV) sulphate solution and 0·5 ml of a saturated solution of sulphamic acid. The solution was reduced at 0·66 V *vs* SCE under a blanket of argon gas until the cell current had decreased to 30 μA. The solution was then oxidized at 1·02 V *vs.* SCE until the cell current had decreased to 30 μA. By using the integrated current consumed during the oxidation, the amount of neptunium titrated was calculated by Faraday's law for a one-electron oxidation.

Uranium procedure

A 7-ml volume of mercury was used as the working electrode, and 10 ml of 0·5*M* sulphuric acid supporting electrolyte were transferred to the titration cell. The solution was deaerated for 3 min with a stream of argon gas. The solution was prereduced at 0·085 V *vs.* SCE under an argon blanket until the cell current had decreased to 50 μA, and was then reduced at −0·325 V *vs.* SCE until the cell current had again decreased to 50 μA. The integrated current consumed during the reduction was recorded as the background. An aliquot containing from 1·0 to 6·0 mg of uranium, was transferred to the titration cell, followed by 0·25 ml of 0·05*M* cerium(IV) sulphate solution. The solution was again prereduced at 0·085 V *vs.* SCE under a blanket of argon until the cell current had decreased to 50 μA. The solution was then reduced at −0·325 V *vs.* SCE until the cell current had decreased to 50 μA. The uranium content was calculated from the integrated current consumed during the last reduction. A correction for the background current was applied.

Calibration

The coulometer was calibrated absolutely[6] for neptunium titrations and relatively[8] for uranium titrations with a 5·014 mg/ml uranium standard solution. Five aliquots were titrated coulometrically, and a relative standard deviation (RSD) of 0·15% was obtained.

DISCUSSION

Neptunium

To be certain that the system was operating properly for the neptunium determination, a 5·344 mg/ml neptunium nitrate solution was titrated. Five titrations were made by the procedure above. The average relative error was +0·07%, and the RSD was 0·21%.

It appeared from a study of the uranium and neptunium potentials that uranium should not interfere with the neptunium determination. Six titrations, by the neptunium procedure described, were then made to determine whether uranium would interfere. Various ratios (1:1 to 100:1) of uranium to neptunium were titrated, and the results are shown in Table I. The average relative error

TABLE I.—RECOVERY OF NEPTUNIUM IN THE PRESENCE OF URANIUM

U present *mg*	Np, *mg*		Relative error %
	Present	Found	
4·761	5·344	5·354	+0·19
4·761	5·344	5·335	−0·17
4·761	0·534	0·532	−0·37
4·761	0·534	0·535	+0·19
47·61	0·534	0·535	+0·19
47·61	0·534	0·537	+0·56

was +0·10%, and the RSD was 0·32%. These results indicate that neptunium can be titrated successfully in the presence of uranium and are in good agreement with previously published results.[5]

Uranium

After the coulometer had been calibrated, a second uranium standard solution was titrated to check the calibration. This second uranium standard solution had a value of 4·763 mg/ml. Five titrations were made by the uranium procedure described. The average relative error was −0·02%, and the RSD was 0·22%.

A study of the uranium and neptunium potentials indicated that if any neptunium(IV) or neptunium(VI) were present during the uranium titration, the neptunium would interfere with the uranium determination. The neptunium(VI) interference can be eliminated by a prereduction titration. The neptunium(IV) interference was eliminated by the addition of cerium(IV) sulphate solution which oxidizes the neptunium to neptunium(VI). The interference which would be caused by the neptunium(VI) and the excess of cerium(IV) is eliminated by the prereduction titration.

The neptunium solution used in this investigation was titrated according to the procedure of Stromatt[5] to determine which neptunium oxidation states were present. It was found that the neptunium was 93·56% (VI), 4·98% (V), and 1·46% (IV).

Five uranium titrations were made in the presence of neptunium by the procedure above except that no cerium(IV) sulphate solution was added. The average relative error was +0·26% (Table II). Five additional uranium titrations were made following the uranium procedure including the addition of the cerium(IV) sulphate. The average relative error for these five titrations was +0·03% (Table III).

TABLE II.—RECOVERY OF URANIUM STANDARDS IN THE PRESENCE OF NEPTUNIUM WITHOUT THE CERIUM(IV) SULPHATE ADDITION

Np present, *mg*	U, *mg*		Relative error %
	Present	Found	
5·344	4·763	4·775	+0·25
5·344	4·763	4·785	+0·46
5·344	4·763	4·771	+0·17
5·344	4·763	4·777	+0·29
5·344	4·763	4·770	+0·15
		Average	+0·26%

TABLE III.—RECOVERY OF URANIUM STANDARDS IN THE PRESENCE OF NEPTUNIUM WITH THE CERIUM(IV) SULPHATE ADDITION

Np present, *mg*	U, *mg*		Relative error %
	Present	Found	
5·344	4·763	4·760	−0·06
5·344	4·763	4·775	+0·25
5·344	4·763	4·763	±0·00
5·344	4·763	4·760	−0·06
5·344	4·763	4·765	+0·04
		Average	+0·03%

It is apparent from these results that cerium(IV) sulphate must be added to the uranium sample to oxidize any neptunium(IV) which may be present. This step has been incorporated into the uranium procedure.

Interferences

There are only a few ions which will significantly interfere with the neptunium titration. These

TABLE IV.—RESULTS OF CONTROLLED POTENTIAL COULOMETRIC TITRATION OF URANIUM–NEPTUNIUM ALLOYS

Np found, %	Average, %	U found, %	Average, %
		99·3	
0·816		99·2	
0·817	0·817	99·2	99·2
		99·2	
0·814		99·3	
0·818	0·816	99·1	99·2
		99·1	
0·818		99·2	
0·820	0·819	99·1	99·1
		99·1	
0·823		99·0	
0·825	0·824	99·1	99·1

are gold, platinum, mercury, thallium, and chloride at concentrations of 0·1*M* or greater. Plutonium and palladium will cause only slight interference.

The number of ions which would interfere with the uranium titration is greatly reduced by the prereduction step. This step will eliminate the interference from the more electropositive ions, such as iron(III), neptunium(VI), plutonium(IV), and cerium(IV). Ions that are more electronegative than uranium will not cause interference. The ions which will interfere are those which will react at the cathode during the uranium titration, namely antimony(III), bismuth(III), copper(I), and molybdenum(VI).

CONCLUSIONS

The results have shown that neptunium and uranium can be determined by controlled potential coulometry in the presence of each other. The procedures outlined above have been used to determine the concentrations of uranium and neptunium in uranium–neptunium alloys. The results of these titrations are presented in Table IV.

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Summary—A controlled potential coulometric titration method has been developed for the determination of neptunium and uranium in the presence of each other. The recovery of a neptunium standard in the presence of uranium was 100·02% with a relative standard deviation of 0·13%, and the recovery of a uranium standard in the presence of neptunium was 100·03% with a relative standard deviation of 0·13%.

Zusammenfassung—Eine coulometrische Titrationsmethode bei konstanter Spannung wurde zur Bestimmung von Neptunium und Uran nebeneinander entwickelt. Die Ausbeute bei einem Neptuniumstandard neben Uran war 100,02% mit einer relativen Standardabweichung von 0,13%, die Ausbeute bei einem Uranstandard neben Neptunium 100,03% mit einer relativen Standardabweichung von 0,13%.

Résumé—On a élaboré une méthode de titrage coulométrique à à potentiel contrôlé pour le dosage du neptunium et de l'uranium en présence l'un de l'autre. Le rendement d'un étalon de neptunium en présence d'uranium a été de 100,02 pour cent avec un écart type relatif de 0,13 pour cent et le rendement d'un étalon d'uranium en présence de neptunium a été de 100,03 pour cent avec un écart type relatif de 0,13 pour cent.

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Application of isotopic exchange for the determination of tin in nickel

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RECENTLY a method was described for the determination of several impurities, namely copper, arsenic, antimony, bismuth and zinc, in nickel cathodes.[1,2] In further experiments the possibility of separating tin from the nickel matrix by isotopic exchange has been investigated.

The principle of radiochemical separation by isotopic exchange is based on the well-known fact that the exchange taking place between the dissolved radioactive ions of an element and its fairly insoluble precipitate is such that the major fraction of the radioactive ions will be eventually bound in the precipitate. In spite of the simple technique and speed of the process, isotopic exchange has seldom been applied in activation analysis for the separation of the components of the irradiated sample. Its application in connection with activation analysis was tried first by Sunderman and Meinke[3] who studied the isotopic exchange between radioactive silver ions and inactive silver chloride. Recently Qureshi and Shabbir[4,5] performed experiments on the radiochemical recovery of cobalt and antimony by means of isotopic exchange.

Isotopic exchange seemed for several reasons to be particularly convenient for the separation of tin from irradiated nickel samples. It was found to be more effective, the lower the solubility of the inactive precipitate used for the exchange. In the case of tin, tin(IV) oxide seemed to be the most suitable precipitate. Metallic nickel dissolves rapidly in nitric acid, taking only 1–2 min in hot nitric acid, while in hydrochloric or sulphuric acid a long time is required for dissolution. On the other hand the solubility of tin(IV) oxide in nitric acid is sufficiently low to obviate precise neutralization of the solution or removal of nitrate ions, and because the metals which form hydroxide precipitates are less likely to be bound on its surface good selectivity can be achieved.

EXPERIMENTAL

The experiments were performed with the ^{125m}Sn isotope (9·5 min half-life).

The irradiations were carried out in the pneumatic facility built into the core of the VVR-S reactor. The stoppered small danamid capsule containing the sample was put into an outer danamid ampoule, then irradiated for 3 min. After irradiation, conveying the sample to the laboratory and unpacking it took about 45–60 sec.

^{125m}Sn was quantitatively determined by measuring the 0·33 MeV photopeak intensity. For the measurements a 3 in. × 3 in. Tl-activated NaI crystal and 256-channel pulse-height analyser were used.

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^{125m}Sn was quantitatively determined by measuring the 0·33 MeV photopeak intensity. For the measurements a 3 in. × 3 in. Tl-activated NaI crystal and 256-channel pulse-height analyser were used.

The isotopic exchange technique was as follows: solid tin(IV) oxide was added to the hot tin solution, then boiled for 1 min. The solution was cooled rapidly and filtered through a G4 glass filter. After washing, the activity of the precipitate was measured on the filter.

Because the way in which the tin(IV) oxide is prepared may influence the effectiveness of the isotopic exchange, it is described: 10 ml of tin(IV) chloride were diluted to 100 ml with water and cooled in ice, then concentrated ammonia was added until a bulky precipitate of hydrated tin(IV) oxide was formed. Subsequently it was heated on a water-bath for 1 hr, then left standing overnight. The precipitate was filtered off, washed with water, dried and ignited for 1 hr at 800°. The cooled product was suspended in water, filtered off on a G3 glass filter and washed with water to remove the very tiny particles. The tin(IV) oxide remaining on the filter was dried, and portions of it were used for experiments.

To determine the most favourable conditions for the separation of tin by isotopic exchange the following experiments were carried out.

Effect of nitric acid concentration. Runs were performed in 4 + 1, 1 + 1, 1 + 4 and 1 + 9 dilutions of nitric acid with water and also with distilled water alone. About 10^4-cpm tin activity was added to 10-ml fractions of these solutions, and then 200 mg of tin(IV) oxide were used for isotopic exchange. The experimental results are summarized in Table I. As can be seen from the table, the 1 + 9 dilution seems to be the most suitable, the recovery of the radioactive tin being almost complete, while at the same time the slight acidity of the solution is favourable for the selectivity of the separation.

Minimum amount of tin(IV) oxide necessary. About 10^4-cpm ^{125m}Sn activity was added to 10 ml of hot nitric acid solution (1 + 9) and the isotopic exchange was performed with 5, 10, 100, 200 and 300 mg of tin(IV) oxide. The experimental results are summarized in Table II. Although with 50 mg of tin(IV) oxide almost complete recovery of radioactivity can be achieved, in the following experiments 200-mg portions were used to minimize the error due to losses during the filtration.

TABLE I.—VARIATION OF RECOVERY OF ^{125m}Sn WITH HNO_3 CONCENTRATION

HNO_3 water ratio	Recovery of ^{125m}Sn, %
4:1	76
1:1	80
1:4	92
1:9	99
water	99

TABLE II*.—VARIATION OF RECOVERY OF ^{125m}Sn WITH WEIGHT OF SnO_2 USED

SnO_2, *mg*	Recovery of ^{125m}Sn %
5	80
10	96
50	99
100	99
200	99
500	99

* The results given in the tables are reproducible to 2–3% for the same preparation of SnO_2.

Selectivity. About 50 mg of nickel were irradiated for 3 min and dissolved, and the isotopic exchange was performed. The activity of the tin(IV) oxide precipitate differed only to a small extent from the background activity, proving the separation for nickel to be satisfactorily selective.

The selectivity of the method for some trace components has been investigated. For this purpose an experimental run was performed in each case in the presence of about 10^4-cpm activity of the element investigated. Tin(IV) oxide was not contaminated by Co, Mg, Zn, Na, K and Cl ions; Mn and Cu showed a contaminating effect of less than 1% of the original amounts. Arsenic, in the absence of carrier, was adsorbed to the extent of 50–60 %, and in the presence of a carrier the extent of adsorption decreased (in the presence of 3, 7 and 15 mg of arsenic carrier the amounts of adsorbed arsenic were 5–6%, 3% and 2–2·5% respectively).

An error can be introduced by titanium when present in amounts equal to or greater than that of the tin, since it is partly adsorbed on tin(IV) oxide and its γ-ray energy is very close to that of tin ($E = 0{\cdot}32$ MeV, $t_{\frac{1}{2}} = 5{\cdot}8$ min). Titanium, in the absence of carrier, was adsorbed to the extent of more than 10% but in the presence of carrier the adsorption decreased (in the presence of 4 mg and 11 mg of carrier 6–8% and 4–5% respectively was adsorbed).

Calibration curve. When known quantities of labelled tin from 10 μg to 100 μg were isotopically exchanged in 10 ml of nitric acid (1 + 9) with 200 mg of tin(IV) oxide, 30 ml of water, being used for washing, the experimental points exhibited ± 3% deviation from a straight line calibration curve.

Reproducibility. A nickel sample containing a known amount of tin was analysed as follows: 50 mg of nickel containing 80 μg of tin were irradiated for 3 min, then dissolved by heating in 2 ml of nitric acid (1 + 1) and diluted to 10 ml with hot water. Then 200 mg of tin(IV) oxide were added to the boiling solution, the boiling was continued for 1 min, and the solution was cooled in ice. After filtering the precipitate was washed with 30 ml of cold water and then counted. About 7–8 min elapsed from the end of the irradiation to the beginning of the counting. For three parallel determinations the deviations from the actual value were ± 3%.

CONCLUSION

Isotopic exchange between solid tin(IV) oxide and dissolved radioactive tin ions seems to be suitable for the separation of tin from a nickel matrix. By this method the recovery of radioactive tin is more than 99% complete, which is adequate for activation-analysis.

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Summary—A method for the determination of tin in nickel by activation analysis is described. Isotopic exchange is used for the separation of tin from nickel. The most favourable conditions for the separation have been determined, under which more than 99% of the tin can be recovered in 7–8 min.

Zussamenfassung—Eine aktivierungsanalytische Methode zur Bestimmung von Zinn in Nickel wird beschrieben. Zur Zinn-Nickel-Trennung wird der Isotopenaustausch angewandt. Die vorteilhaftesten Bedingungen zur Trennung wurden ermittelt; mit ihnen können mehr als 99% des Zinns in 7–8 Minuten abgetrennt werden.

Résumé—On décrit une méthode pour le dosage de l'étain dans le nickel par analyse par activation. On utilise l'échange isotopique pour séparer l'étain du nickel. On a déterminé les conditions les plus favorables pour la séparation, dans lesquelles plus de 99 pour cent de l'étain peuvent être récupérés en 7–8 mn.

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ANNOTATION

The meaning of "sensitivity" in trace analysis

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IN CHOOSING a method for trace analysis, if elements or compounds that could interfere are absent or can be removed or masked, if the species to be determined can be concentrated to only a limited degree or not at all, and if a reasonably wide selection of analytical tools is available, then the choice of method is usually best made by deciding which analytical method will detect the least amount of the species. This decision is seldom easy, principally because trace methods for most materials except the elements[1] have not been critically compared. Even so, when the chemist attempts, by studying the literature, to find the method that will detect the least amount, he is discouraged by the fact that various terms are used for expressing how little material an analytical method will detect.

It is the purpose of this paper to explore the expressions for "sensitivity" and related terms, and to attempt to establish a common ground on which analytical methods can be compared. It has not proved possible to devise a universal definition. Rather, generalized definitions are proposed, which, though not universal, can be modified to fit the particular requirements of each method.

Fundamental concepts

Critical examination of the literature of analytical chemistry reveals a confusion not only of terms, but also of concepts, regarding "sensitivity." Most elementary textbooks of analytical chemistry do not treat the subject at all, while the specialized reference texts on colorimetry, electrochemistry, spectroscopy, chromatography, and trace analysis seldom devote more than a few lines to a definition of terms. In general, recent textbooks of gas–liquid chromatography provide the most satisfactory discussions.[2]

In the texts and papers that were examined,[1-18] the authors did not agree on the nomenclature describing "sensitivity," but they did generally agree on basic concepts. Two concepts seem to be necessary and sufficient:

(1) the ratio of the change in the output signal produced by an increment of the material to be determined to that increment, and

(2) the smallest quantity of material that can be detected "with certainty."

A definition of the term "with certainty" will be presented later in this paper. The two concepts are inter-related in that (2) cannot be stated without first defining (1).

General definitions

In naming concepts (1) and (2), the choice of terms should be made after considering two factors: scientific accuracy, and most common current usage. When most chemists speak of the "sensitivity" of a chemical method, they usually mean "How small an amount can be determined?" This is very similar to concept (2). However, in most recent textbooks, concept (1) is called "sensitivity", while concept (2) is assigned the name "lower limit of detection", "smallest detectable quantity", "limit of detection", "detectable limit", or some similar term.

It is proposed then, to call concept (1) "sensitivity", and concept (2) "detectability", the first on the basis of current usage in recognized reference texts, and the second on etymological grounds [Latin *detectus*, past participle of *detegere*, to detect, and old French from Latin *habilitas*, aptness (later, state of being able)]. It remains, however, to express these terms in precise mathematical language so that they may be useful to chemists.

Chemists have used a variety of definitions of terms relating to sensitivity and detectability. Morrison[1] describes two approaches. One was devised by Kaiser and Specker[18] in which the "minimum detectable difference" between a reading and a blank is given by

$$I_s - I_b = ks_b\sqrt{2} \qquad (1)$$

where k = constant determined by the degree of confidence required
s_b = standard deviation of the blank output signal
I_s and I_b = output signals for the sample and blank, respectively.

They recommend that k should be $2\sqrt{2}$ which corresponds to confidence limits above 99%, whereas the ASTM[10] has recently proposed that a signal difference of one standard deviation is sufficient [equivalent to $k = 1/\sqrt{2}$ in equation (1)].

In Morrison's other approach, suitable for smaller numbers of observations, the blank and sample signals are treated as pairs, and the standard deviation s_d is calculated from a suitable statistical relationship.

Wilson[11] also assumed that two readings were taken, one of the sample and one of the blank. By assuming that the standard deviations of the sample and blank readings are the same, he arrived at a "criterion of detection" (detectability) of $1{\cdot}645S_0$ for confidence limits of 95%, where S_0 is the standard deviation of the difference between the sample and blank readings (and corresponds to $s_b\sqrt{2}$).

Roos[12] proposed the concepts of "Criterion of Detection" and "Limit of Detection." He also pointed out that two concepts are involved, "error of the first kind" that is met by Wilson's criterion, and an "error of the second kind" that is met by the criterion of $3{\cdot}390S_0$. The error of the first kind entails the risk of assuming that the material is present when it is not, and the error of the second kind entails the risk of assuming that the material is absent when it is not.

The difference in readings between a sample and a blank is a useful concept for many analytical methods, such as colorimetry, but not for others, such as gas chromatography. Different theoretical approaches to the problem yield slightly different factors that relate the standard deviation and the degree of confidence to the detectability. Some approaches utilize the standard deviation of the blank while others use the standard deviation of the sample. Different confidence limits are used, but most agree on the 95% confidence limits, or 1·96 times the standard deviation.

Sensitivity

A precise definition of sensitivity is relatively easy to produce. We may write

$$S_n = \left(\frac{\Delta I}{\Delta Q}\right)_{Q_n} \tag{2}$$

where S = sensitivity
ΔI = the change in the output signal, I, in suitable units
ΔQ = the increment of material, in suitable units, that produced ΔI

$$Q_n = \frac{Q_2 + Q_1}{2} \text{ where } Q_2 - Q_1 = \Delta Q.$$

The units of sensitivity will be determined by the units in which ΔI and ΔQ are expressed. It follows, therefore, that the sensitivities of two different analytical methods cannot be compared unless ΔI and ΔQ are expressed in the same or related units for the two methods. Defining measurement of S at $Q = Q_n$ is necessary in the event that I is not linearly related to Q.

Another important concept is the "limiting sensitivity", S_0;

$$S_0 = \lim_{Q \to 0} \left(\frac{\Delta I}{\Delta Q}\right). \tag{3}$$

This quantity may be evaluated by calculating ΔI as a function of ΔQ, and extrapolating to $Q = 0$ graphically, or by fitting the data to an equation and solving it for $Q = 0$. The limiting sensitivity is required for defining the detectability.

Detectability

Translation of concept (2), now called "detectability", into mathematical language, is difficult because of the ambiguity implicit in the term "with certainty." Chemists have used a variety of definitions of this concept. Consideration of the approaches that have been taken by others suggests that the most useful definition of detectability is

$$D = \lim_{Q \to 0} \left[\frac{2s_I}{\left(\frac{\Delta I}{\Delta Q}\right)}\right] \tag{4}$$

where s_I = standard deviation of I at $Q = Q_n$.
If s_I is independent of I, then equation (4) becomes

$$D = \frac{2s_I}{S_0}. \tag{5}$$

The factor "2" in the equation actually has no theoretical significance; it is similar in magnitude to the various factors that have been used. No theoretically derived factor can be more useful because the difficulty inherent in measuring s_I for some systems may require that this quantity be estimated from other independent measurements.

Equation (5) is nearly the inverse of the relationship used by Mandel and Stiehler[13–15] in their "sensitivity criterion"; it differs in that $2s_I$ is used in place of s_I. Because it has the units of "amount" rather than "amount^{-1}", as in the Mandel–Stiehler relationship, it has more practical meaning to the analytical chemist. Equation (5) is also very similar to the expression for "limit of detection" as derived by Dal Nogare and Juvet,[2] who assumed a linear relationship between the output signal and the concentration, and used R_n, the peak-to-peak noise level, instead of s_I. In gas chromatography, R_n is certainly easier to measure than s_I because the signal is displayed on a recorder as a function of time. In general, however, R_n will be smaller than s_I; it will approach s_I as the time interval is extended.

Applications

These criteria will prove useful to analytical chemists only if they can be meaningfully used in defining the limitations of most analytical methods. Consequently, they have been applied to spectrophotometry and to gas–liquid chromatography, in order to demonstrate how two different analytical methods can be compared. A similar approach can be taken for other methods.

In spectrophotometry, it is convenient to express the sensitivity, S, in absorbance units per milligram, or A mg^{-1}. In gas–liquid chromatography, however, S is usually stated in the units mV ml mg^{-1}. Dimbat, Stross, and Porter[17] have proposed an expression for evaluating S directly from the chromatogram. As the units for I are different in the two cases, it is not possible to compare the sensitivities of the two methods directly. It should be noted that in evaluating S for the two methods, studies should be made to determine whether the relationship between I and Q is linear.

To compare the two methods directly, we must use the detectability criterion, as expressed in equations (4) and (5), and hence, the standard deviation, s. As stated previously, in gas–liquid chromatography the peak-to-peak signal-to-noise value approaches s as the time increases. Any deviations produced by non-reproducible introduction of the sample into the column are not included in this correlation, but in practice these are usually very small compared to other deviations. The standard deviation of a spectrophotometric method is usually obtained by making repeated measurements on a standard sample. Care must be taken to include or minimize errors due to mechanical positioning of the cell, differences between cells, volumetric errors, *etc.*

Assume then that a spectrophotometric method for methanol has a limiting sensitivity $S_0 = 0{\cdot}010\ A$ mg^{-1}, while for a particular gas chromatographic method, $S_0 = 0{\cdot}02$ mV ml mg^{-1}. Assume also that the standard deviation for the spectrophotometric method is $0{\cdot}005\ A$, while for the gas chromatographic method $R_n = 2\ \mu$V ml. Then $D_{spect.} = 1$ mg, while $D_{glc} = 0{\cdot}2$ mg. Hence, the gas–liquid chromatographic method will detect "with certainty" one-fifth the quantity of methanol that is detected by the spectrophotometric method.

The detectability criterion for the comparison of analytical methods must be applied with care because the limiting sensitivity may depend on the volume of sample that can be analysed, *e.g.*, the analysis of solutions by spectrophotometry, or it may depend on the rate at which the material passes through the transducer, *e.g.*, thermal conductivity cells in gas chromatography. Morrison[1] has discussed this problem for liquids, while Halasz[20] has discussed it for gas chromatographic detectors. In the example, the limiting sensitivity of the spectrophotometric method should have been qualified by stating the volume for which it was determined, and that for the gas chromatographic method should have included complementary information regarding the mass and flow conditions under which the detector was operated.

Conclusion

This treatment indicates that while the sensitivities of analytical methods cannot usually be compared, the detectability as defined in this paper can be used to determine which analytical method will detect with certainty the smallest amount of a material.

In order to permit the comparison of the detectabilities of analytical methods, authors should report the limiting sensitivity and the standard deviation of a single measurement. The experimental conditions that restrict the limiting sensitivity, and consequently the detectability, should be clearly stated. If the standard deviation of a single measurement cannot be measured, information regarding the noise level should be reported.

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Summary—The concepts of the ratio of the change in output signal produced by an increment of a material to be determined to that increment, and the smallest quantity of a material that can be detected "with certainty" are examined. The name "sensitivity" is suggested for the former, and "detectability" for the latter. Mathematical relationships are proposed that will permit the comparison of the detectability of two different analytical methods.

Zusammenfassung—Die Begriffe "Verhältnis der Signaländerung am Ausgang, die durch eine Vergrößerung der Menge des zu bestimmenden Stoffes hervorgerufen wird, zu der Mengendifferenz" und "kleinste Menge eines Stoffes, die mit Sicherheit nachgewiesen werden kann" werden untersucht. Der Name "Empfindlichkeit" wird für den ersten, "Nachweisbarkeit" für den zweiten Begriff vorgeschlagen. Es werden mathematische Beziehungen angegeben, die den Vergleich der Nachweisbarkeit bei zwei verschiedenen analytischen Methoden gestatten.

Résumé—On a examiné les concepts du rapport du changement dans le signal de rendement produit par un incrément d'une substance à doser à cet incrément, et de la plus petite quantité d'une substance que l'on peut détecter "avec certitude". On suggère le nom "sensitivité" pour le premier et "détectabilité" pour le second. On propose des relations mathématiques qui permettront la comparaison de la détectabilité pour deux méthodes analytiques différentes.

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LETTER TO THE EDITOR

Remarks on hexamminecobalt(III)carbonatoberyllate

SIR,

The letter of Vinagradov[1] on this subject requires a number of comments from me.

Because of the large proportion of water in the compound the avoidance of a dehydrating agent—even as mild a one as absolute ethanol—as a wash liquor seemed to us to be a minimum reasonable precaution in preparing samples for analysis. We therefore used 60% ethanol and, as noted in the paper,[2] dried the precipitate by suction. In all cases constant weight was reached in 15–20 minutes and the material was in equilibrium with atmospheric water vapour, as was indicated by the subsequent very small weight changes when exposed to atmospheres of controlled humidity. Generally, the observations indicated that the atmospheric humidity was between 32 and 80%, but on one occasion the air must have been drier than usual as the compound gained 0·1% after exposure to 32% relative humidity. It is therefore clear that there is no substance in Vinagradov's suggestion that the wash-liquor was not removed in these experiments. This fact is also evident from the close agreement between the cobalt contents of the four precipitates prepared on different occasions. Subsequent experience with acetone, or 95% ethanol followed by ether, has shown that these are also valid (and quicker) methods of drying the precipitate; this could not be assumed in our work.

Vinagradov criticises our procedure of conditioning to a definite humidity as being likely to be protracted. Since the humidity suggested would be one within the normal atmospheric range, and the samples would be in equilibrium with the prevailing atmospheric humidity, the time required for reaching constant weight would be expected to be quite short. In our experiments speed was not important and the samples were generally left overnight. In practice the time could be minimized by the use of reduced pressure. On general grounds it is desirable that a gravimetric precipitate should be exposed to an atmosphere with humidity controlled at a value appropriate to the particular compound. The use of an empty desiccator under reduced pressure, as described by Vinagradov, is open to criticism because the compound supposedly being conditioned has, in fact, to supply the water vapour in the enclosed volume. In the present instance this treatment would be expected to give an atmosphere drier than those used in our experiments (32–80% relative humidity). As we showed that the water content of the compound varies continuously between 10·8 and 11·1 molecules (per formula unit) within these humidity limits it might be expected that Vinagradov's treatment would dry the compound to a water content of less than 10·8 molecules. Nevertheless his assertion that the compound contains 10 molecules of water, seeming to imply that it is a definite hydrate, needs more convincing experimental evidence than has so far been forthcoming. (It should also be noted that if it were a precise decahydrate the factor for conversion to beryllium would be 0·03942, not 0·0395 as stated by Vinagradov.)

Table I shows the results of various analyses of the compound by Vinagradov *et al.*[3] Sen Gupta,[4,5] and Monk and Exelby.[2] The number of water molecules per formula unit has been calculated, in each case, from the result of the determination of a particular element or group. The uncertainty limits have been calculated from the limits of error quoted by the authors where available. In the case of Monk and Exelby the results of only the cobalt analyses have been quoted as this determination was specifically chosen for the purpose because of its high accuracy. The limits of error here correspond to the standard deviation of the mean. The table includes data from Sen Gupta's second paper[5] in which his methods of preparation of three varieties of the compound, (*a*) needle-shaped crystals, (*b*) tetrahedral crystals and (*c*) polyhedral crystals, are described. On the basis of the analytical results for Be, N, C and H, Sen Gupta claims that (*a*) contains 11, and (*b*) and (*c*) 10 molecules of water. In his original paper[4] (*a*)-type crystals are referred to as "feather-like" and stated to contain 12 molecules of water. Analytical results from both papers are given in Table I.

None of these results can be considered to provide evidence of a definite hydrate under any of the conditions of preparation. Vinagradov's results considered altogether provide as much evidence for a water content of about 11 molecules as they do for the 10 molecules he claims; this is true for his cobalt determination, which has the smallest relative error of his four sets of analyses and which gives a mean result quite close to ours.

TABLE I.—WATER CONTENT OF PRECIPITATE, CALCULATED FROM PUBLISHED DATA

Author	Method of treating precipitate	Number of molecules of water per formula $[Co(NH_3)_6]_3[Be_4O(CO_3)_6]$								Remarks
		Calculated from determination of								
		Claimed	Co	Be	N	C	CO_3	H	H_2O	
Vinagradov, Apirina and Cherstvenkova[3]	Alcohol, ether suction and 15 mins in moderate vacuum with no desiccant	10	10·9 ± 0·4	$10·0^{+0·7}_{-0·6}$	—	—	$10·8^{+1·1}_{-1·0}$	—	10·1 ± 0·5	Be-content of precipitate was estimated from the original weight of beryllium and final weight of precipitate.
Sen Gupta[4,5]	Alcohol and air-drying	10	—	10·4	10·3	10·7	—	9·8	—	Precipitated from potassium bicarbonate solution. Types (*b*) and (*c*).
		12	—	12·2	12·3	12·9	—	10·6	—	Precipitated from ammonium carbonate solution. Type (*a*).
		11	—	12·2	11·4	11·1	—	10·1	—	
Monk and Exelby[2]	60 % alcohol, suction to constant weight. Constant weight at:									
	32% R.H.	10·8	10·77 ± 0·01	—	—	—	—	—	—	
	55% R.H.	11·0								
	80% R.H.	11·1								

Sen Gupta's preparations were air-dried and would therefore be expected to reflect the atmospheric humidity at the time of preparation but the variation in his results is much greater than would be expected from this cause alone. While it might appear that precipitation from potassium bicarbonate gives a product containing less water than precipitation from ammonium carbonate the figures are hardly sufficiently accurate to substantiate any definite hydrate. Our tentative suggestion that the variation in water content with humidity might be accounted for by varying proportions of two hydrates does not now seem very plausible. An alternative explanation is that the compound has a zeolite structure.

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TALANTA REVIEW*

COMPLEXATION REACTIONS OF DITHIOCARBAMATES

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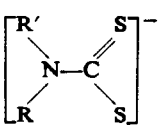
Summary—The complexation reactions of various disubstituted dithiocarbamates are discussed. Special attention is paid to studies of composition and stability of various metal complexes. The conditions of complex formation in solution are treated in terms of side-reaction coefficients. The properties of metal–dithiocarbamate complexes are presented as a function of the nature of the substituents in the ligand molecule.

THE analytical applications of dithiocarbamates have been discussed in several textbooks and monographs on trace analysis,[1] colorimetry,[2] organic reagents,[3,4] extraction,[5] and in special papers,[6] but there is no comprehensive treatment of the properties of various complexes and their composition and stability, although numerous analytical methods are based on these reagents. A large amount of information is contained in an excellent monograph on dithiocarbamates[7] published in 1962, but the analytical aspects are not sufficiently emphasized.

The purpose of this review is to discuss critically the complexing properties of various dithiocarbamates and the composition and stability of the complexes formed, in relation to their analytical application. No attempt has been made to include all references which deal with analytical application of dithiocarbamates, but attention has been focused on those which contribute some new information on the problem of dithiocarbamate complexes.

GENERAL REMARKS ON DITHIOCARBAMATES

The complexing properties of dithiocarbamates are directly connected with the presence of two donor sulphur atoms, which primarily determine the nature of the metals that can be bound, and the strength of the complexes formed. In the dithiocarbamate ion



R′ and R denote various organic substituents, which do not influence significantly the metal–sulphur bonding, but may determine some analytical properties of the

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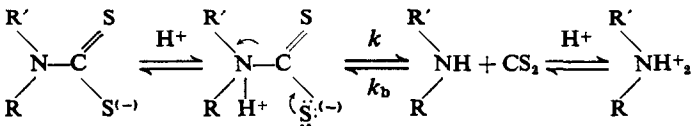
complexes. Most of the analytically interesting properties occur with disubstituted dithiocarbamates. Monosubstituted compounds are less useful because of their stronger reducing properties and tendency to decompose to hydrogen sulphide.[8]

The general method of preparation of dithiocarbamates from carbon disulphide and amines in alkaline medium is probably one of the reasons for the widespread incorrect nomenclature of these compounds. Thus a compound obtained from pyrrolidine and carbon disulphide is frequently named as pyrrolidinedithiocarbamate, whereas it is more correctly named pyrrolidine-*N*-carbodithioate, *N*-dithiocarboxy-pyrrolidine or *C*-tetramethylenedithiocarbamate.[9] The first two correct names do not emphasize the presence of the most characteristic complexing group. The third name, in spite of the lack of direct connection with the amine used in the synthesis, seems to be the most useful. In this review this nomenclature will be used, abbreviated where necessary to the symbol DTC as a general symbol for dithiocarbamates in cases where no confusion may occur.*

For the analyst, the most important property of the dithiocarbamate ion is its protonation in acidic solution and the subsequent decomposition into carbon disulphide and the protonated amine. Several authors report the values of pK_a of various dithiocarbamic acids, and those which correspond to aqueous solutions are given in Table I. From the kinetic and dissociation constants it follows[10,11] that the decomposition proceeds through the dipolar ion according to the scheme:



and is favoured when the pH of the medium is lower than pK_a for the $R'RNH_2^+$ ion. The rate-limiting step of this reaction is the decomposition of the dipolar ion. Contrary to these observations Soni and Trivedi[12] found the diethyldithiocarbamate ion to be a diacidic base. However, their results significantly differ for data calculated previously on the assumption that the ion is a monoacidic base. In non-aqueous solutions the dithiocarbamic acids are generally soluble and much more stable,[16,17] which has led to numerous applications in the extraction of metal chelates from acid solutions.

The rate of decomposition of dithiocarbamates in acid solution has been studied polarographically[10,14,18] by measuring the decrease of the anodic wave of dithiocarbamate. Similar results may be obtained spectrophotometrically[19–22] by measuring the absorbance of the dithiocarbamate at 360 mμ or that of the cobalt complexes at 650 mμ. In the range where pH $\gg pK_a$ of the DTC acid, the decomposition proceeds according to the equation $V = -k[H^+]C_{DTC}/K_a$ where k is the true rate constant, V the velocity, and C_{DTC} the total DTC concentration. When pH $\ll pK_a$ the decomposition rate is independent of the pH of the solution and $V = -kC_{DTC}$. The former equation is usually valid in the range over which measurements are performed and therefore the apparent rate constant k/K_a is usually given as a measure of the decomposition rate. Often for characterization of the acid the pH value is given at which the half-life of the DTC is 10 hr. Both methods should give consistent results

* The older German name is *Carbaminat* (*e.g.*, in Malissa and Gomišček[99]) and the new nomenclature uses *Carbamidat* (*e.g.*, in Bode *et al.*[16,20]).

TABLE I.—pK_a VALUES OF SOME DITHIOCARBAMIC ACIDS IN AQUEOUS SOLUTIONS

Acid derived from	pK_a	Reference
Dimethylamine	3·66	11
Diethylamine	4·04	11
	3·95	10
	7·5 (pK_{a_1})?	12
	8·4 (pK_{a_2})?	
Di-n-propylamine	4·79	11
Di-n-butylamine	5·19	11
Pyrrolidine	2·95	10
Morpholine	5·2	10
	5·19	15
Aminoacetic acid	4·57	14
	3·12 (pK_{a_1})*	13
	3·84 (pK_{a_1})	

* One of the pK_a values corresponds to the carboxyl group.

when over the range investigated and discussed the decomposition proceeds according to the same equation. Data given in Table II were recalculated in both ways. In certain cases they exhibit significant discrepancies, probably because of differences in ionic strength, temperature, *etc.*

The decomposition of dithiocarbamates in acid solution, a drawback in most analytical procedures, has been exploited for the determination of these compounds.[7,23–26] The most rapid procedures are based on acid and alkaline titration of the sample.[27,28]

TABLE II.—APPARENT RATE CONSTANTS k' FOR DITHIOCARBAMATE DECOMPOSITION, AND pH VALUES FOR HALF-LIFE TIMES $\tau_{1/2} = 10$ hr (AT ~20°C)

Dithiocarbamate derived from	k' $l\ mole^{-1}\ min^{-1}$	pH (for $\tau_{1/2} = 10$ hr)	Ref.
Dimethylamine	2000	6·24*	10
Diethylamine	8000	6·84*	10
	10,200*	6·95	20
Di-n-propylamine	110	4·98*	10
	8100*	6·85	20
Di-isopropylamine	300,000	8·42*	10
Di-n-butylamine	140	5·09*	10
Methyl-n-butylamine	2400	6·32*	10
Pyrrolidine	11	3·98*	10
	25*	4·35	20
Piperidine	2800	6·40*	10
	6500*	6·75	20
Morpholine	8900	6·89*	20
Methylglucosamine	7200*	6·8	20
Pyrrolidine-2-carboxylic acid	160*	5·15	20
Iminodiacetic acid	1200	6·03*	21
Diethanolamine	11,800	7·01*	22
Aminoacetic acid	7·2*	3·8	20
	34	4·8*	14
Sodium cyanamide	41,000*	7·55	20

* Values calculated from data given in the reference.

COMPLEX FORMATION WITH DIFFERENT METALS

The dithiocarbamate ligands have two donor sulphur atoms able to react with those metals[29] which form insoluble sulphides. This general statement is only approximately true because chelate and steric effects also influence the reaction.

The water-insoluble metal dithiocarbamates, and aqueous solutions of many soluble ones, have characteristic colours, which are widely used for analytical purposes. The colours depend only slightly on the nature of the substituents in the disubstituted dithiocarbamate,[21,30–33] and may be different for monosubstituted ligands[34–37] or dithiocarbamates derived from acid amines.[38] This is probably due to the possibility of thiono-thiolo-tautomerism or the presence of other reactive donor groups in the ligand molecule. The absorption spectra of water-insoluble dithiocarbamate–metal complexes in organic solvents such as chloroform have been studied.[39,40]

Most metal complexes may be represented by the formula $M(DTC)_n$ where n is equal to the charge of the metal ion. If the co-ordination number of the metal is twice its charge such complexes are neutral molecules. The bidentate ligand forms a four-membered chelate ring, as shown by X-ray measurements.[41–43]

The composition $M(DTC)_n$ was established by special studies[6,44–48] and confirmed by numerous applications in titrimetric and gravimetric methods. The same component ratio has also been found for soluble complexes.[49] The dithiocarbamates are monomeric, except for the copper(I) complexes of diethyl and dipropyl derivatives, where tri- and tetrameric structures respectively, have been demonstrated.[50,51] Polymeric chelates of another type were found for the piperazine derivative, which contains two CS_2 groups, at two ends of the heterocyclic ring.[52]

A more complicated situation exists when complexes are formed with metal ions which have different oxidation states and/or do not form simple solvated ions in aqueous solutions. Among these are Ti, V, Nb, Cr, Mo, W, U, Re, Pt-metals, As, Sb, Sn, Se and Te.

According to some investigators[32,53–55] titanium forms a yellow complex of unknown structure, but others do not support this observation.[30,40]

The vanadium complex has the peculiar property of being extracted with methyl isobutyl ketone at pH 2 or 6, with an intermediate range where no extraction occurs.[56] This suggests that the oxo-cations VO_2^+ or VO^{3+} react with the ligand,[17] but reduction to lower oxidation states is also possible, taking into account that both vanadium(IV) and (V) react with dithiocarbamate.

Of the proposed[57,58] formulae of the niobium complex, $NbO(DTC)_3$ and $Nb(DTC)_3$, the former has been shown correct.[59–61] Data on the tantalum complexes are very scarce[62] and do not allow conclusions be made about their structure.

In the case of chromium(III) the inertness of its compounds affects its reactivity. DTC complex formation is achieved by reduction of chromium(VI)[54] or at elevated temperature.[30] For the diethyl derivative the formula is $Cr(DTC)_3$,[57,63] which confirms the older studies of Malatesta.[64]

The reactivity of 16 various dithiocarbamates towards molybdenum was studied by Kulberg and Kovaleva,[65] who found that in faintly acid and neutral solution a yellow compound is precipitated, and a violet one from warm 1*M* hydrochloric acid solution. To both groups of compounds the composition $MoO_3(HDTC)_2$ was ascribed. The yellow form has been found by many authors[30,31,40,38] but there is only one other report of the formation of the violet form,[66] and it has been argued that

the yellow form, in the case of pyrrolidine derivative, has the composition $Mo(DTC)_3$.[57] The recent extraction experiments of Shustova[67] indicate that the Mo:DTC ratio is 1:2 and on this basis the formula $MoO_2(DTC)_2$ was proposed. It differs from $MoO_3(HDTC)_2$[65] by one water molecule, which may be ascribed to the uncertainty of elemental analysis. A similar composition was found by Byrko[62] for the pyrazoline derivative.

There are only incomplete data available about the yellowish tungsten complex.[31,53]

The uranium(VI) complexes of dithiocarbamates which do not contain hydrophilic groups differ from other complexes of these ligands by their solubility in water. Malatesta[64] reported the formula as $UO_2(DTC)_2$ while Zingaro[68] stated the existence of the ion $UO_2(DTC)_4^{2-}$ in solution, and the compound $UO_2(DTC)_2 \cdot K_2UO_2(DTC)_4$ in the solid state.

In these compounds the diethyldithiocarbamate ion may function as a mono- and a bidentate ligand. For the hexamethylenedithiocarbamate Prodinger[69] found the metal–reagent ratio 1:3; Malissa and Kolbe-Rohde,[57] however, report the ratio 1:6.

Some controversies exist about the complexes of rhenium. Probably in strongly acid solutions of perrhenates the extractable dithiocarbamate complexes are formed.[53,62]

For the platinum metals the existence of various oxidation states and the formation of many stable and often inert complexes interfere with the study of dithiocarbamate compounds. Unquestionable is the formation of the yellow $Pd(DTC)_2$ complexes.[30,31,40,46,70,71] Platinum(II) forms in acid solution easily extractable complexes,[30,40,71] but platinum(IV) reacts incompletely,[30,31,40] possibly with partial reduction to the bivalent state. Heterometric studies[72] indicate the presence of platinum complexes having the metal to ligand ratios 1:1, 2:3, 1:2 and 1:3. Those complexes probably also contain chloride ions. The yellow rhodium(III) complex $Rh(DTC)_3$[73] may be extracted with dichloroethane[71,74] or 4-methyl-2-pentanone.[75] Even less is known about ruthenium, which probably forms $Ru(DTC)_2$,[70] and iridium reactions, which are slow and need special precautions.[30,31,40]

Many authors[30,31,34,40] indicate the formation of yellow–brown complexes of gold(III), the composition of which was established heterometrically as corresponding to metal–reagent ratios 1:1, 2:3 and 1:2.[46] However Tulupa and Usatenko[76] report reduction to gold(I), which subsequently forms a 1:1 complex.

Arsenic, antimony and tin in their lower oxidation states give relatively stable complexes,[30,77] but except for the reaction of arsenic(V) with the morpholine derivative[31] no compounds are reported for arsenic(V) and antimony(V). This is presumably because of the high stability of the oxy-anions over a wide pH range and the instability of dithiocarbamates in very acid solution. For tin, beside the yellow[39,40,78] or white[30] complex of tin(II) formed at $pH < 9$, a complex of tin(IV) is formed at $pH < 6$. A more detailed study should indicate whether there exist DTC compounds of arsenic, antimony and tin in their higher oxidation states, or whether reduction occurs.[48]

From weakly acidic solutions of selenium(IV) a dithiocarbamate is precipitated[30,31,38,40,44] but no details of its structure are given. Its formula is proposed as $Se(DTC)_2$.[79–81] A similar compound was found for tellurium,[79] when the relatively stable $Te(DTC)_4$[44,82] was reduced with thallium(I).[83] In alkaline solutions this

complex $Te(DTC)_2$ (which is intensely orange in carbon tetrachloride solution) disproportionates into Te(O) and Te(IV).

Information about the composition of various metal dithiocarbamates may presumably be found in the patent literature, but in general is of limited analytical interest.

In the case of several metals which have different oxidation states the formation of dithiocarbamate complexes is accompanied by redox reactions. The best known examples are manganese(II), iron(II) and cobalt(II) which undergo oxidation to the tervalent state[30,31,33,34,40,62] or even for manganese to the quadrivalent state.[84] This behaviour is connected with the high polarizability of the dithiocarbamate ligands. In strongly reducing media it is sometimes possible to obtain less strongly coloured compounds of bivalent ions. Gleu and Schwab[30] indicate that for the dithiocarbamate derivatives of diethylamine, piperidine, thiazane, dimethylamine, pyrrolidine, morpholine and piperazine the ability to stabilize higher oxidation states decreases in the order given. Some exceptions to this order may be attributed to differences in the physical structures of the precipitates.

In contrast the thallium(III) compounds are easily reduced to thallium(I) complexes,[85] indicating the low stability of complexes of 18-electron type ions.

The reducing properties of dithiocarbamates cause several ions (e.g. permanganate and dichromate) to be readily reduced to lower oxidation states.[7] Presumably such reactions interfere with the formation of complexes of molybdenum(VI),[20,67] vanadium(V), niobium(V),[58] platinum metals and tin(IV). Bode *et al.*[20] have stated that reduction may also interfere in the complexation of silver, gold, mercury, thallium, selenium, tellurium and iron. The reduction rate depends on pH and the nature of the substituents in the ligand molecule. The strongest reducing properties are associated with monosubstituted derivatives and the disubstituted derivative of *N*-methylglucosamine.

From these data it follows that dithiocarbamate ligands complex metal ions having partly filled *d* orbitals, ions with filled *d* orbitals but low positive charge, and ions with an 18+2 electronic structure. Thus they react with the elements from titanium to selenium (except germanium), niobium to tellurium and tungsten to bismuth.

THE EFFECT OF SUBSTITUENTS IN THE LIGAND MOLECULE

For many years after the early work of Delepine[86] only the dimethyl and diethyldithiocarbamates were used in chemical analysis. They form complexes with many metals, insoluble in water but soluble in organic solvents. To widen the applicability of these reagents attempts have been made to introduce new substituents with better analytical properties. Taking into account the properties of the complexes formed, it is possible to divide the dithiocarbamate reagents into three groups:

(*i*) dithiocarbamates having hydrophobic substituents, which give water-insoluble complexes, extractable with organic solvents;

(*ii*) dithiocarbamates containing hydrophilic groups, *i.e.*, OH^- or COOH, which form metal complexes soluble in water but insoluble in organic solvents and therefore not extractable;

(*iii*) dithiocarbamates containing two donor CS_2^- groups, which form polymeric chelates insoluble in all solvents.

This classification deals primarily with disubstituted compounds but may be extended to monosubstituted derivatives.

The first group includes a great number of studied compounds. The analytical applications of the dithiocarbamates—derivatives of dimethylamine and diethylamine[1–3,6]—have been described in several hundreds of papers. The derivatives of dipropylamine[30,87–90] and dibutylamine[91] have also been studied. Derivatives of aromatic and heterocyclic amines such as dibenzylamine,[71,92–95] diphenylamine,[71] cyclohexylethylamine,[96] pyrrolidine,[30,38,54,56–59,71,97–99] piperidine,[30,32,59,71,73,74,100] hexamethyleneamine,[69,85,100–102] morpholine,[30,31] thiazane,[30] indole[103] and substituted pyrrolidines[62,104] have similar properties. There are no significant differences in the chelating properties of these compounds. Comparative studies indicate small differences in the logarithms of the copper chelate stability constants[89,90] (less than 2 log units) wavelength of the absorption maximum (432–435 mμ) and molar absorptivity of these chelates[105] (12·1–13·4 $\times$ 10^3). Also the character of the precipitate,[30] rate of precipitation or dissolution in organic solvents[98] and the completeness of extraction[71] do not differ greatly.

Substituents exert a significant effect on the rate and degree of oxidation of metals forming dithiocarbamate complexes.[30] For example diethyldithiocarbamate strongly promotes manganese oxidation, whereas the thiazane derivative precipitates manganese(II) in the presence of even weak reducing agents.

For a particular analytical purpose a given ligand is preferred, but other properties of the reagent such as ease of synthesis and purification, stability both in the solid and in solution, must be taken into account. Therefore, for example, the pyrrolidine derivative is widely used when acidic media are recommended.

Dithiocarbamates of this group are mostly used as the sodium or ammonium salts, but in extraction methods the compounds soluble in organic solvents are often used, *e.g.*, diethylammonium diethyldithiocarbamate or zinc dibenzyldithiocarbamate. The first of these two reagents was introduced by Wyatt[106,107] and investigated in detail by Bode and Neumann.[16,17] These studies have shown its advantages over the sodium salt in extraction from acid solutions.[108,111] The second reagent[71,92,93,95,112] is also soluble in organic solvents and the low thermodynamic stability of the zinc complex enables fast and complete metal exchange reactions with other metals forming more stable complexes.

The second group of dithiocarbamates having hydrophilic substituents has not been investigated so thoroughly. Because of the presence of OH or COOH groups the metal complexes are soluble in water and do not dissolve readily in organic solvents. Because of steric factors and the rather weak complexing properties of the OH and COOH groups compared with those of the CS_2^- group it follows that the complexes formed have similar structure and properties to those of the first group. However, the complexation occurs in one phase and therefore the presence of successive complexes is easily observed.

Diethanoldithiocarbamate was introduced by Serfass *et al.*,[113,114] who, like others,[115,116] used it for masking several metals in the determination of zinc, or stripping of mercury into the aqueous phase.[117] This reagent was also found useful for direct colorimetric determination of cobalt,[118] molybdenum and uranium,[33] copper,[119] and nickel, cobalt and copper mixtures,[120,121] and for indirect determination of

mercury and cyanides.[122–124] With TBP the complexes of bismuth, copper and nickel and tellurium may be extracted.[125]

At higher concentrations the solubility of the complex is too low, and so Bode *et al.*[20] have also investigated dithiocarbamates synthesized from pyrrolidine-2-carboxylic acid, *N*-methylglucosamine, sodium cyanamide and aminoacetic acid (monosubstituted DTC). In all cases the solubility was good but the first-mentioned reagent seems to be the most advantageous because its reducing ability is low and stability in acidic solutions rather high. In spite of their reducing properties the monosubstituted dithiocarbamates have found several analytical applications in the colorimetric determination of bismuth and copper,[34] nickel and cobalt[126] and masking in complexometric titrations.[127] These ligands are more resistant to acids but at low pH values where the carboxylic group is undissociated the metal complexes may precipitate.

To this group also belongs bis(carboxymethyl)dithiocarbamate, investigated by Hulanicki *et al.*[21,49] This reagent is less susceptible to oxidation than the diethanolamine derivative and is quite stable in acidic solution. It is used for colorimetric determination of copper, nickel and cobalt[22] and masking of various metals in the dithizone determination of zinc.

Malissa and Miller[103] have investigated dithiocarbamates containing sulphonate groups, derivatives of diphenylamino-4,4′-disulphonic acid and *p*-aminosulphonic acid but report that the metal chelates are not readily soluble in aqueous media.

The third group of dithiocarbamates is represented by the piperazine derivative,[30,105] which contains two CS_2^- groups. This reagent was investigated by Hulanicki and Shishkova,[52] who found that its chelates are insoluble in water and numerous organic solvents. This suggests a polymeric structure of the chelates, which probably form chains with not more than 10 members. Other bis-dithiocarbamates were also prepared (*e.g.*, from polymethylenediamines[128]) but nothing is known about their complexing properties and analytical applications.

On the basis of these observations it may be stated that each of these groups of dithiocarbamate reagents finds its special analytical application. The first group of dithiocarbamates without hydrophilic substituents is applicable in colorimetric determinations where the coloured complex is extracted by organic solvents. Nevertheless many determinations may also be carried out in aqueous pseudo-solutions stabilized with protective colloids. In trace analysis these reagents are used for concentration of small amounts of metals by extraction or precipitation before their determination by various instrumental methods. Because dithiocarbamates are "wide spectrum" reagents this procedure is often used when numerous trace elements are to be determined in a material which does not contain heavy metals as main components.

The second group of hydrophilic reagents may find applications in direct colorimetry in aqueous solutions and for masking metals, for example in extraction or precipitation. In these methods the complexation with dithiocarbamate proceeds in homogeneous conditions. Therefore a relatively greater excess of the reagent is needed. It is obvious that they may be used only in alkaline, neutral and slightly acidic solutions.

The bis-dithiocarbamates, which form the last group, can be used in colorimetry in pseudo-solutions, and in the concentration of metals by precipitation.

As already mentioned, the monosubstituted dithiocarbamates may find their place in any of these groups, depending on the characteristics of their complexes, but their application is severely limited by their reducing properties and tendency to precipitate metal sulphides.[8,129]

THE EFFECT OF SOLUTION COMPOSITION ON COMPLEXATION

Numerous experimental data on the formation of dithiocarbamate complexes enable a clear picture to be obtained of conditions under which these complexes may be formed. Nevertheless in order to understand the nature of these reactions several factors must be separately discussed:

(*i*) formation of hydroxo-complexes of metals with increasing pH;
(*ii*) formation of metal complexes with ligands added as buffers, to prevent precipitation of hydroxides or to increase selectivity;
(*iii*) protonation of dithiocarbamate ions, which leads finally to decomposition of the ligand.

In most cases stepwise formation of dithiocarbamate complexes may be neglected, owing to a rather drastic shift of the equilibrium towards precipitation or extraction of the metal chelate.

In a simple case of a precipitated 1:1 complex, Ringbom's expression[130] for the conditional solubility product

$$K_{so}' = [M'][DTC']^n = [M][DTC]^n \cdot \alpha_M \alpha_{DTC}^n$$

(where α_M and α_{DTC} are the side-reaction coefficients) gives a straightforward answer, that precipitation occurs quantitatively when $K_{so}' < 10^{-7}$, and the reaction is masked when $K_{so}' > 10^{-2}$. For more complicated cases the masking coefficient[131] may be a useful concept. Its most general form[197], for the compound M_jA_i, is

$$pM' = \frac{1}{j} pK_{so} - \log \alpha_M + \frac{i}{j} (\log[A'] - \log \alpha_A)$$

and gives the relationship between the solubility product K_{so}, concentration of the precipitating anion [A'], and the side-reaction coefficients $\alpha_M = [M']/[M]$, $\alpha_A = [A']/[A]$ for the cation and anion, respectively. [M'] denotes the total concentration of all species of M in solution, and [M] the concentration of the free ion; [A'] and [A] have corresponding meanings. When this equation is used under the condition that

$$[A'] = \frac{i}{j} [M']$$

a simpler expression is obtained:

$$pM = \frac{1}{j+i} [pK_{so} - i \log j/i] - \frac{j}{j+i} \log \alpha_M - \frac{i}{j+i} \log \alpha_A$$

which was discussed in detail previously.[131] The conclusion follows that $pM' > 6$ represents complete precipitation, $pM' < 3$ represents masking.

To characterize the systems in which precipitation of metal dithiocarbamates may or may not occur the changes of individual coefficients should be considered.

The coefficient $\alpha_A = \alpha_{DTC}$ depends mainly on protonation of basic groups. As the dithiocarbamic acids are in general not very weak acids, in the pH range 6–14 $\alpha_{DTC} = 1$. In more acidic media the kinetic factors of dithiocarbamate decomposition play a significant role.

The coefficient α_M is the sum of all coefficients for different side-reactions of the metal ion. The principal interfering reactions are formation of hydroxo-complexes, and formation of other complexes with buffer or masking substances. The coefficient $\alpha_{M(OH)} = \sum_0^f \beta_f[OH]^f$ is a function of [OH] only (for mononuclear complexes), and therefore strongly increases with increasing pH. The coefficient $\alpha_{M(X)} = \sum_0^g \beta_g[X]^g$ is constant as long as the concentration [X], of free ligand additionally complexing the metal ion, is constant. However, in the case of complexing agents having basic properties, when the pH decreases the concentration of the free ligand decreases very significantly, causing a decrease in $\alpha_{M(X)}$. Thus, independent of the relative values of $\alpha_{M(X)}$ and $\alpha_{M(OH)}$, the pH increase over a broad range is responsible for the increase of the conditional solubility product of metal dithiocarbamates. This is the opposite of the general rule for organic precipitants, which are stronger bases than dithiocarbamates and hence the change in α_A predominates over the changes in α_M.

This conclusion is in agreement with the experimental observation that at higher pH values only those dithiocarbamate complexes which have extremely small molar solubility are precipitated, *i.e.*, those of mercury, silver, copper, cadmium, lead and nickel. On this basis Gleu and Schwab[30] have described a metal separation scheme based on precipitation of diethyldithiocarbamates at different pH values (Table III).

Extraction of dithiocarbamate complexes with organic solvents proceeds according to the equation

$$M^{n+} + n\,DTC^- \rightleftharpoons \{M(DTC)_n\}_O$$

where the subscript O denotes species in the organic phase. The extraction constant K_e of this reaction is equal to the product of the complex formation constant β_n in the aqueous phase and the partition constant $P_{M(DTC)_n}$

$$K_e = \beta_n \cdot P_{M(DTC)n} = \frac{[M(DTC)_n]}{[M][DTC]^n} \cdot \frac{[M(DTC)_n]_O}{[M(DTC)_n]} = \frac{[M(DTC)_n]_O}{[M][DTC]^n}$$

From the analytical point of view it is convenient to consider the total concentrations of metal-containing species in both phases and therefore the introduction of conditional constants is advantageous. The extraction coefficient E_M of the metal, expressed with the aid of the corresponding side-reaction coefficients,[22] is given by the equation

$$\log E_M = \log K_e + \log \alpha_{MR_n} - \log \alpha_M + n(\log [R'] - \log \alpha_R)$$

where α_{MR_n} represents the side-reaction coefficient of the complex (here of the $M(DTC)_n$ complex) in the organic phase, α_M is, as before, the side-reaction coefficient of the metal ion in the aqueous phase, [R'] the total concentration of unbound ligand (*i.e.*, DTC) and α_R its side-reaction coefficient. When $\log E_M > 3$ the extraction is practically complete, when $\log E_M < -2$ the metal is practically completely masked.

In this equation, which has a similar form to that for precipitation reactions, the first term corresponds to the true equilibrium constant of the reaction, and the

second ($\alpha_{M(DTC)_n}$) may be assumed to be unity, though in fact its value is unknown, and presumably it may be included in the numerical value of the extraction constant. The coefficient α_M is exactly the same as before, with $n = i/j$, but α_R—beside the $\alpha_{R(H)}$ component—contains an additional term $\alpha_{R(org)}$ which describes the extraction of the ligand itself. Its value is usually greater than that of $\alpha_{R(H)}$ and therefore plays a decisive role in the whole equilibrium. In the case of diethyldithiocarbamic acid, from the data of Bode[19] it follows that

$$\alpha_{DTC(CCl_4)} = 1 + \frac{V_{CCl_4}}{V_{H_2O}} [H^+] \times 1{\cdot}6 \times 10^6.$$

Thus at pH > 7·5 its value is practically equal to 1.

From these considerations it is seen that the effect of side-reactions on both precipitation and extraction is similar. These conclusions are experimentally confirmed by the similarity of the conditions in which both processes occur and therefore the scheme of separation by extraction closely resembles that for precipitation

TABLE III.—METAL IONS REACTING WITH DITHIOCARBAMATES IN VARIOUS MEDIA[30,38,44,133,156]

Complexing agent	pH ~ 5–6	pH ~ 9	pH > 11
Tartrate	Ag, As, Bi, Cd, Co, Cu, Fe, Hg, In, Mn, Ni, Pb, Pd, Sb, Se, Sn, Te, Tl, Zn	Ag, Bi, Cd, Co, Cu, Fe, Hg, In, Mn, Ni, Pb, Pd, Sb, Te, Tl, Zn	Ag, Bi, Cd, Co, Cu, Hg, Ni, Pb, Pd, Tl, Zn
EDTA	Ag, As, Bi, Cd, Cu, Fe, Hg, In, Mn, Pb, Pd, Sb, Se, Sn, Te, Tl	Ag, Bi, Cu, Fe, Hg, Pd, Sb, Te, Tl	Ag, Bi, Cu, Hg, Pd, Tl
KCN	—	Bi, Cd, Fe, In, Mn, Pb, Sb, Te, Tl	Bi, Cd, Pb, Tl
Citrate + EDTA	—	Ag, Bi, Cu, Hg, Sb, Te, Tl	—

(Table III). In this table some other common complexing media are also included to give a more complete picture of the analytical possibilities of separation with dithiocarbamates. Chalmers and Dick[132] suggest extraction of dithiocarbamates in the group separation of cations by extraction.

Several other complexing and masking solutions should also be mentioned. Ammonium citrate seems promising for the masking of iron, indium and manganese.[133–135] Iron(III) may also be masked by pyrophosphate,[6,135] sodium sulphosalicylate[136–138] and hydrofluoric acid,[108] whereas the fluoride ions at pH 6 mask the extraction of niobium but do not interfere with the iron(III) reaction.[59,139] In weakly acidic solutions oxalates prevent the reaction of gallium[140] and titanium.[55] Tiron (disodium pyrocatechol-3,5-disulphonate)[141] has interesting complexing properties in respect to iron and manganese, making it possible to separate these elements from bismuth, cadmium, cobalt, copper, nickel, lead and zinc. 1-(2-Pyridylazo)-2-naphthol masks zinc perfectly and does not influence the reaction of cadmium.[142] 1,10-Phenanthroline, however, masks iron, manganese, nickel and zinc, making possible the determination of lead.[143]

A separate problem is presented by reactions in acid solution. In these conditions the α_A coefficient has the most significant effect, indicating the protonation of the ligand and its subsequent decomposition. The kinetics of this latter process seem to be most important in the formation and decomposition of the complexes in acid solution. While in such media precipitation is rarely used, several authors apply extraction from acid solution,[17,53,97,99] using the diethylamine and pyrrolidine derivatives.

A very important parameter in these extractions, *e.g.*, from 10*N* sulphuric acid,[17] 6*M* hydrochloric acid,[97,99] 10*M* hydrochloric acid,[144] is the choice of the proper organic solvent, which influences the partition of the dithiocarbamic acid and its stability.[16] To decrease the rate of ligand decomposition it is often advantageous to replace the sodium or ammonium salts of dithiocarbamates by salts soluble in organic solvents, *e.g.*, diethylamine diethyldithiocarbamate.[16,17,110] Good results may also be obtained when the diethyldithiocarbamate is replaced by tetramethylenedithiocarbamate,[97,99] which is decomposed more slowly in acids. Usatenko and Tulupa[144] give the order of diethyldithiocarbamate complex decomposition with increasing acid concentration as zinc, cadmium, lead, bismuth, iron, nickel, copper (cobalt does not decompose). This indicates that the path of decomposition is not only a dissociation of complex followed by acid decomposition of free ligand.

Various solvents have been examined, *e.g.*, ethers, alcohols, esters, pyridine, hydrocarbons and halogenated hydrocarbons.[98,145,146] The most advantageous are halogenated hydrocarbons and aliphatic esters. Šedivec and Flek[145] indicate that the usefulness of solvents increases in the series: benzene, carbon tetrachloride, chloroform, ether, butyl acetate and ethyl acetate, but this sequence does not correspond to the increasing solubility of metal chelates.[98,146]

The solubility is usually greatest in chloroform and pyridine and much smaller in benzene, toluene, carbon tetrachloride and ethyl acetate. The polar halogenated hydrocarbons (ethylene chloride, 1,2-dichloroethylene, trichloroethylene, chlorobenzene and chloroform) are better than the non-polar (carbon tetrachloride, perchloroethylene).[147]

The choice of the solvent to some extent depends on the nature of the metal complex. The water-soluble uranyl complex is extracted with n-butanol,[148] methyl ethyl ketone,[149] isopentanol or ethyl ether, but not with chloroform or carbon tetrachloride.[40] The general rule for complexes of oxo-cations is to extract them with ketonic solvents.[56] Obviously when the ligand molecule contains hydrophilic groups extraction occurs only slightly or not at all, unless special solvents, such as acetate esters[149] or tributyl phosphate[125] are used.

In analytical practice several other properties of solvents are of importance (density, emulsion formation, purity, chemical inertness, *etc.*) and therefore ethyl acetate,[53] chloroform[39] and carbon tetrachloride[44,150] are widely used.

A detailed study of several parameters which do not enter into the equilibrium equations was performed by Šedivec and Flek.[145] They confirmed the previously observed fact[157] that in the presence of an excess of the ligand the extraction is not complete. This was especially observed for chloroform, carbon tetrachloride and benzene extractions and presumably is connected with stabilization of dispersed colloid particles by the dithiocarbamate anion, in a way similar to that observed for gelatin or soap. This effect may be suppressed by addition of neutral salts, which

increase the effectiveness of extraction.[145,152,153] Probably the increase of the extraction rate in acid solutions is connected with decomposition of the stabilizing anion adsorbed on the surface of the chelate particles.[145] Nevertheless the data given by different authors for the extractions often disagree.

STABILITY SERIES OF CHELATES

Difficulties in the determination of absolute values of stability constants of dithiocarbamate complexes stimulated several authors to establish the stability series based on solubility or extraction. Malatesta[154] found the solubility of diethyldithiocarbamates decreased in the order Tl(I), As(III), Zn, Fe(III), Ni, Cd, Pb, Co(III), Cu(II), Ag(I), Hg(II). This corresponds approximately to the solubilities of the sulphides. A similar series was given by Podtchainova[6] but neither of these authors indicates clearly the conditions of formation of the chelates. Potentiometric titration of metal ions with diethyldithiocarbamate[155] has given a similar series—Zn, Cd, Pb, Ni, Cu, Ag—but with an indication that this corresponds to non-complexing media, so this sequence may be closely related to the real solubilities of the complexes.

Wickbold[156] has shown that the presence of weak complexing agents—tartrate and ammonia (pH 9) or tartrate at pH 12—does not alter significantly the sequence [except for the strongly complexed iron(III)] namely, Fe(III), Mn(II), Zn, Sb(III), Tl(III), Cd, Bi, Pb, Co, Ni, Cu, Ag, Hg. The order of the first four relates to pH 9 only.

These relative solubilities agree well with the solubility products determined by Kemula and Hulanicki[22,143,157,158] and Starościk and Siagło.[159]

There is a similar lack of data for extraction procedures. The metal ion replacement in non-aqueous solutions of dithiocarbamate proceeds quantitatively if

$$\{K'_{e[M(DTC)_n]}\}^m \gg \{K'_{e[M'(DTC)_m]}\}^n$$

where K_e' represents the conditional extraction constant of the complex indicated. Eckert[160] established the replacement series of ions ("*Verdrängungsreihe*") valid in strictly defined solution conditions (pH 5·6, chloroform). However, this series, Mn, [As(III), Zn], [Sn(II), Fe(III)], Cd, Pb, Bi, [Ni, Co(II)], Cu, Ag, Hg, may be applied to diethyl- and tetramethylenedithiocarbamates and does not depend on the solvent (chloroform, carbon tetrachloride).

The experiments of Bode and Tusche[150] with precipitated metal hydroxides or carbonates at pH 8·5 or 11 were performed in easily reproducible conditions, at a constant metal ion concentration defined by their solubility products. With carbon tetrachloride as solvent they obtained the sequence Mn, Te(IV), Fe(III), Sb(III), In, Zn, Tl(I), Cd, Co(III), Pb, Bi, Ni, Tl(III), Cu, Ag, Pd(II), Hg(II), in which the ions up to indium react only at pH 8·5, whereas the others also react at pH 11.

A slightly different sequence was given by Tulupa *et al.*[149] for diethanoldithiocarbamates extracted with ethyl acetate: Mn(II), Zn, Ni, Co, Cd, Fe(III), Pb, Bi, Cu, Ag, Hg, Au(III). The differences may be attributed to the effect of the hydroxyl group in the ligand.

In all equilibria between dithiocarbamates and metal ions, especially in heterogeneous systems, the slow attainment of equilibrium plays an important role. This is particularly true for reactions of iron(III), nickel, cadmium and other ions.[150,160] The presence of various complexing agents has a significant influence on the rate of exchange reactions.

Another important factor in these processes is the possibility of a redox reaction

TABLE IV.—ANALYTICAL APPLICATIONS OF METAL EXCHANGE REACTIONS OF DITHIOCARBAMATE COMPLEXES, ACCORDING TO THE EQUATION $nM + mM'(DTC)_n \rightleftharpoons nM(DTC)_m + mM'$

M	M'(DTC)$_n$	Solvent	Medium	Application	Reference	
Hg^{2+}	Cu(diethyl.DTC)$_2$	CCl_4	citr., pH 4·5	indirect col. detn. of Hg	117, 165, 166	
		$CHCl_3$	pH 5	end-point in merc. titr.	169, 170	B, C
		butyl acetate	$HgCl_2$ soln.	compl. detn. of Cu	175	
		CCl_4	—	indirect titr. of Hg	181	
		ppt.	—	indirect detn. of Hg	182	
	Cu(diethanol.DTC)$_2$	aq.	pH 4·5	indirect col. detn. of Hg	123	
Ag^+	Cu(diethyl.DTC)$_2$	CCl_4	NH_3, pH 11	indirect compl. detn. of Te	82	A
		C_6H_6	NH_3, citr., pH 8	indirect col. detn. of Ag	172	
		$CHCl_3$	EDTA, pH 3·7	extr. titr. of Ag	171	
		ppt.	—	compl. indirect detn. of Ag	183	
	Bi(diethyl.DTC)$_3$	CCl_4	NH_3 EDTA, pH 9·5	indirect polar. detn. of Ag	168	
Cu^{2+}	Bi(diethyl.DTC)$_3$	$CHCl_3$	tartr. KCN, NaOH	indirect col. detn. of Bi	180	
	Pb(diethyl.DTC)$_2$	$CHCl_3$	pH $\leqslant$ 4	col. detn. of Cu	185	
		$CHCl_3$	tartr. pH 5·5	col. detn. of Cu	186	
		$CHCl_3$	citr.	col. detn. of Cu	163	
		$CHCl_3$	pH 4·8	col. detn. of Cu	164	
		$CHCl_3$	NH_3, citr.	col. detn. of Cu	132	
		$CHCl_3$	pH 5	indirect titr. of Pb	170	C
		CCl_4	tartr., KCN, pH 12	indirect. col. detn. of Pb	176, 180	
	Cd(diethyl.DTC)$_2$	$CHCl_3$	pH 5	indirect titr. of Cd	169	B

	Tl(diethyl.DTC)	$CHCl_3$	tartr., KCN, NaOH	indirect. col. detn. of Tl	180	
	$Zn(dibenzyl.DTC)_2$	CCl_4	H_2SO_4	col. detn. of Cu	92, 93, 95, 112	
		CCl_4	0·25 M HCl	col. detn. of Cu	162	
	$Zn(diethanol.DTC)_2$	aq.	citr. pH 4·5–10	col. detn. of Cu	125	
	$Sb(diethyl.DTC)_3$	CCl_4	—	col. detn. of Sb	40	
	$Se(diethyl.DTC)_2$	CCl_4	—	col. detn. of Cu	81	
	$Te(diethyl.DTC)_4$	CCl_4	NH_3, pH 11	indirect compl. detn. of Te	82	A
	$M'(diethyl.DTC)_n$	$CHCl_3$	citr., pH 12	col. detn. of Pb, Bi, Cd, Zn, Mn, Fe	174	
Tl^{3+}	$Pb(diethyl.DTC)_2$	CCl_4	KCN, pH 13	radiom. detn. of Pb	177	D
	$Zn(dibenzyl.DTC)_2$	CCl_4	0·01–5 N H_2SO_4	col. detn. of Tl	94	
Bi^{3+}	$Zn(diethanol.DTC)_2$	aq.	citr., pH 5·5–9·5	col. detn. of Bi	125	
Co^{3+}	$Zn(diethanol.DTC)_2$	aq.	citr., pH 5·5–9·5	col. detn. of Co	125	
	$Zn(diethyl.DTC)_2$	$CHCl_3$	NH_3, tartr., pH 10·5	radiom. detn. of Co	178	
Ni^{2+}	$Zn(diethanol.DTC)_2$	aq.	citr. pH 4·5–10	col. detn. of Ni	125	
Pb^{4+}	Tl(diethyl.DTC)	$CHCl_3$	tartr., KCN, pH 11·5	radiom. detn. of Pb	177	D
Cd^{2+}	$Sb(diethyl.DTC)_3$	$CHCl_3$	tartr., pH 9	separ. of Sb(iodom. detn.)	173	
As^{3+}	$Zn(diethyl.DTC)_2$	$CHCl_3$	2·5 M HCl	substoich. detn. of As	115	
Te^{4+}	$Zn(diethanol.DTC)_2$	aq.	citr. pH 4·5–6·5	col. detn. of Te	125	
Zn^{2+}	$Mn(diethyl.DTC)_2$	$CHCl_3$	pH 5·2	separ. of Mn (col. detn.)	179	
M^{n+}	$Zn(diethyl.DTC)_2$	ppt.	pH 4–5 or 9–10	pur. of Zn salts from heavy metals	184	

Abbreviations: col.—colorimetric, compl.—complexometric, detn.—determination, extr.—extractive, iodom.—iodometric, merc.—mercurometric, polar.—polarographic, pur.—purification, radiom.—radiometric, separ.—separation, substoich.—substoichiometric, titr.—titration, ppt.—reaction involves the precipitate of dithiocarbamate, aq.—reaction in homogeneous aqueous phase.

Methods based on two reactions are indicated by the same letter in the last column.

of the metal ion. A well-known example[133] is the cobalt(III) complex, which is so stable that after its formation no exchange occurs with other ions, even mercury(II), whereas cobalt(II) ions in the aqueous phase react with the weakest complexes such as those of indium or zinc only. The same is true when the action of complexing agents on cobalt(II) ions or cobalt(III) complexes is considered.[120]

The rate of metal ion exchange in a homogeneous system (water-acetone solution, di-n-propyldithiocarbamate complexes) has been studied by Regenass *et al.*[88] They give the stability sequence Zn, Ni, Co, Cu and emphasize the effect of oxidation of cobalt(II) by oxygen. Nickel exchange in a methylcellosolve solution of dithiocarbamates is slow[161] but replacement of nickel by copper is on the contrary a rather rapid reaction, suggested to be S_E2 in type.[87]

In spite of the incomplete data on extractability and stability of complexes, numerous analytical methods are based on metal replacement between a complex of a metal M′ and solvated M ions. These procedures indicate the relative stabilities of the complexes of both metals and from the analytical point of view are of special interest because in combination with a suitable choice of medium they offer excellent methods of selective and specific determination of a particular ion. In Table IV such methods are listed, together with an indication of the reaction conditions for the replacement.

INVESTIGATION OF DITHIOCARBAMATE COMPLEXES IN SOLUTION

The study of dithiocarbamate complex stabilities must take into account some peculiar properties of the ligand and of the complexes formed, namely the possibility of decomposition of the ligand in acidic solution.

Concentrations of the species involved in complexation reactions may be measured directly only in a few cases, where the complexes are substantially dissociated. This procedure was successfully used by Budevsky *et al.*[187] in the study of carboxymethyldithiocarbamate complexes of cobalt by the spectrophotometric method of corresponding solutions. Spectrophotometry was also applied by Usatenko and Fedash[84] in the investigation of manganese(III) complexes, which may be considered as rather weak.

The evaluation of the thermodynamic stabilities of stable complexes in solution may be performed by direct potentiometric determination of metal ion concentration in equilibrium with the complex. This method is, however, restricted to those metals which form sufficiently reversible and reproducible electrodes in solutions of their ions, so is limited to silver and mercury.[143,158]

The most important methods of investigation of stable complexes are based on shifting the main complexation equilibrium by means of some competition reaction. The competition between metal ion and proton for the ligand is often used, but this relatively simple method fails in the case of dithiocarbamate ligands because of the unfavourable nature of the proton–dithiocarbamate reaction. Therefore the following competition methods should be used:

(*i*) competition of two metals for a ligand, one of them forming complexes of known characteristics

(*ii*) competition of two ligands for a metal ion, one being the dithiocarbamate and the other forming complexes of known stability.

The first group of methods includes potentiometric measurements on the system with the indicator electrode working as a third kind of electrode. With a similar electrode Hulanicki[22,143] determined the solubility products of copper, nickel, cadmium, lead, zinc and thallium diethyldithiocarbamates, and Starościk and Siagło[159] that of indium diethyldithiocarbamate. In all these experiments (except that for thallium) additional complexing agents were used to prevent hydrolysis of the excess of metal ions, so the systems involved two competition reactions.

With the second group of competition methods Janssen[89,90,188] determined the complex stabilities in the system dithiocarbamate–copper ions–8-hydroxyquinoline (or 8-hydroxyquinoline-5-sulphonic acid). The results obtained in homogeneous water–ethanol media were extrapolated to purely aqueous solutions. With a heterogeneous system containing a precipitate of the dithiocarbamate copper chelate, Kemula and Hulanicki[157] determined the solubility products of copper, lead and zinc diethyldithiocarbamates, using ethylenediamine, EDTA and NTA, and NTA as competing ligands for copper, lead, and zinc respectively.

A different kind of competition method should be used when the dithiocarbamate complexes are soluble in aqueous media. Hulanicki and Minczewska[49] used dithizone (diphenylthiocarbazone) as a competing ligand and determined the shift of $pH_{1/2}$ for the dithizone extraction of copper, lead, cadmium and nickel, caused by the formation of bis(carboxymethyl)dithiocarbamate complexes in the aqueous phase. The stability of the complexes in this system enabled all experiments to be performed in solutions of sufficiently high pH, so the total concentration of unbound dithiocarbamate could be assumed equal to the free ligand concentration. In this study the excess of the ligand shifted the equilibrium towards the complex with maximum co-ordination number. The stepwise formation of complexes may be indicated spectrophotometrically if smaller concentrations of the ligand are used.[22] The stability constants in these experiments could only be approximately evaluated ($\beta_1 \sim 10^{14}$, $\beta_2 \sim 10^{21}$).

The existence of such successive complexes for ligands having hydrophilic groups was also mentioned by other authors.[20,98,188] For other ligands the presence of such complexes was shown by Janssen,[89,188] working with homogeneous water-ethanol solutions. However in heterogeneous systems (precipitation and liquid-liquid extraction) the equilibrium is so strongly shifted in the direction of the complex having the maximum number of attached ligands that only in special systems can the presence of successive complexes be shown. Usatenko *et al.*[100,189,190,195] have determined amperometrically the equilibrium constant of the reaction

$$2M(DTC)^{+} \rightleftharpoons M(DTC)_2 + M^{2+}$$

using the oxidation current of the $M(DTC)^{+}$ complex as indicator current; they studied the lead, cadmium and zinc complexes of diethyl-, pentamethylene- and hexamethylenedithiocarbamates. The equilibrium constant of the reaction is shifted significantly to the left only for mercury(II). Therefore in non-complexing solutions, unless an equimolar amount of the ligand is exceeded, no mercury–dithiocarbamate precipitates. Using the combined potentiometric (mercury electrode) and solubility methods Kemula *et al.*[158] studied the formation of 1:1, 1:2 and 1:3 complexes. With a similar indicator electrode and procedure the thallium(I) complexes were studied.[22]

The formation of intermediate complexes was demonstrated heterometrically by Bobtelsky *et al.*[45,46,72] in the case of mercury, gold and platinum, but not for lead,

TABLE V.—EQUILIBRIUM CONSTANTS IN THE METAL–DITHIOCARBAMATE SYSTEMS

Metal ion	Method	Temp., °C	Medium	Log of the constant	Ref.
			$C_3H_7NS_2$ Dimethyldithiocarbamic acid		
Cu^{2+}	sp	20	89% EtOH	β_1 15·4, β_2 29·5	90
	sp	20	75% EtOH	β_1 14·4, β_2 27·7	89, 90
	sp	20	51·7% EtOH	β_1 13·2, β_2 25·7	90
	exp	20	0% EtOH	β_1 11·4, β_2 21·7	90
			$C_5H_{11}NS_2$ Diethyldithiocarbamic acid		
Ag^{+}	Ag	25	0·1 KNO_3	K_{so} − 19·6	143
Cu^{2+}	Ag	25	0·1 KNO_3	K_{so} − 29·6	143
	sol	25	0·2 NaCl	K_{so} − 30·2	157
	sp	20	75% EtOH	β_1 14·9, β_2 28·8	89
Zn^{2+}	Ag	25	0·1 KNO_3	K_{so} − 16·9	143
	sol	25	0·1 KNO_3	K_{so} − 17·3	157
	amp	—	—	$(\beta_1^2 K_{so})$ − 8·3	195
Cd^{2+}	Ag	25	0·1 KNO_3	K_{so} − 22·0	143
	amp	—	—	$(\beta_1^2 K_{so})$ − 6·4	195
Hg^{2+}	Hg	20	0·1 KNO_3	K_{so} − 43·5, β_1 22·3	158
	sol	20	0·1 KNO_3	β_2 38·1, β_3 39·1	158
In^{3+}	Ag	20	0·1 KNO_3	K_{so} − 25·0	159
Tl^{+}	Ag	25	0·1 KNO_3	K_{so} − 10·1	22
	sol	25	0·1 KNO_3	β_1 4·3, β_2 5·3	22
Pb^{2+}	Ag	25	0·1 KNO_3	K_{so} − 21·7	143
	sol	25	0·1 KNO_3	K_{so} − 21·9	157
	amp	—	—	$(\beta_1^2 K_{so})$ − 6·0	195
Ni^{2+}	Ag	25	0·1 KNO_3	K_{so} − 23·1	143
	sp	—	—	K_2 4·4	84
			$C_7H_{15}NS_2$ Dipropyldithiocarbamic acid		
Cu^{2+}	sp	20	89% EtOH	β_1 16·1, β_2 31·0	90
	sp	20	75% EtOH	β_1 15·1, β_2 29·4	89, 90
	sp	20	51·7% EtOH	β_1 14·1, β_2 27·6	90
	exp	20	0% EtOH	β_1 12·5, β_2 24·0	90
			$C_9H_{19}NS_2$ Di-n-butyldithiocarbamic acid		
Cu^{2+}	sp	20	75% EtOH	β_1 15·2, β_2 29·4	89
			$C_5H_7O_4NS_2$ Bis(carboxymethyl)dithiocarbamic acid		
Cu^{2+}	dis	20	0·1 KNO_3	β_2 21·5	49
Cd^{2+}	dis	20	0·1 KNO_3	β_2 11·2	49
Pb^{2+}	dis	20	0·1 KNO_3	β_2 15·5	49
Ni^{2+}	dis	20	0·1 KNO_3	β_2 7·9	49
Zn^{2+}	dis	20	0·1 KNO_3	$\beta_2 < 4·5$	49
			$C_5H_9NS_2$ Tetramethylenedithiocarbamic acid		
Cu^{2+}	sp	20	89% EtOH	β_1 14·8, β_2 28·4	90
	sp	20	75% EtOH	β_1 13·9, β_2 26·8	89, 90
	sp	20	51·7% EtOH	β_1 12·6, β_2 24·7	90
	exp	20	0% EtOH	β_1 10·9, β_2 20·8	90
			$C_6H_{10}O_2NS_2$ 3-Carboxy-pentamethylenedithiocarbamic acid		
Cu^{2+}	sp	20	89% EtOH	β_1 16·2, β_2 31·0	90
	sp	20	75% EtOH	β_1 15·1, β_2 29·0	90
	sp	20	51·7% EtOH	β_1 13·9, β_2 26·8	90
	sp	20	0% EtOH	β_1 11·9, β_2 22·4	90
			$C_6H_{10}NS_2$ Pentamethylenedithiocarbamic acid		
Cu^{2+}	sp	20	75% EtOH	β_1 14·7, β_2 28·4	89
Pb^{2+}	amp	—	—	$(\beta_1^2 K_{so})$ − 5·4	133
			$C_3H_5O_2NS_2$ Carboxymethyldithiocarbamic acid		
Co	sp	40	0·1 KNO_3	β_1 3·3, β_2 7·8 β_3 13·3	187

cadmium, bismuth and copper.[191–194] Nevertheless, heterometry does not seem to be a precise method for such investigations. The breaks on the heterometric curves may correspond not only to changes of chemical composition, but also to changes in the physical structure of the precipitate.

The equilibrium constants for different metal–dithiocarbamate systems are collected in Table V, presented in the manner used in the Stability Constant Tables.[196] These data are in good agreement with the previously established stability series or with empirically developed analytical procedures based on relative stabilities of complexes.

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Zusammenfassung—Die Komplexbildungsreaktionen mehrerer disubstituierter Dithiocarbamate werden diskutiert. Besondere Aufmerksamkeit wird Untersuchungen der Zusammensetzung und Stabilität verschiedener Metallkomplexe geschenkt. Die Bedingungen der Komplexbildung in Lösung werden an Hand von Nebenreaktionskoeffizienten abgehandelt. Die Eigenschaften von Metall-Dithiocarbamatkomplexen werden als Funktionen der Natur der Substituenten im Ligandenmolekül angegeben.

Résumé—On discute des réactions de complexation de divers dithiocarbamates disubstitués. On porte une attention particulière aux études relatives à la composition et à la stabilité de divers complexes métalliques. Les conditions de formation de complexes en solution sont traitées en fonction de coefficients de réaction secondaire. On présente les propriétés des complexes métal-dithiocarbamate en fonction de la nature des substituants dans la molécule de ligand.

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DETERMINATION OF POTASSIUM BY AN AUTOMATIC ULTRAVIOLET ABSORPTIOMETRIC METHOD

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Summary—An automatic ultraviolet absorptiometric method has been developed for the determination of potassium. The method involves precipitation of potassium by addition of a known excess of sodium tetraphenylborate, removal of the potassium tetraphenylborate precipitate by filtration, and measurement of the excess of sodium tetraphenylborate in the filtrate by means of its absorbance at 254 mμ. Most of the apparatus, including a continuous filter, is standard AutoAnalyzer equipment but a Uvicord ultraviolet absorptiometer replaces the conventional colorimeter. Build-up of precipitate in the system is eliminated by immersing the mixing coils in an ultrasonic bath which is actuated intermittently by a simple timing mechanism. The method is especially suitable for potassium analysis in production plant where flame photometer results are sometimes affected by fertilizer dust in the air surrounding the burner.

A FULLY automatic laboratory method[1] for the simultaneous determination of ammoniacal nitrogen, nitrate nitrogen, phosphate and potassium in fertilizer solutions has been in use for four years in the laboratories of the Agricultural Division of Imperial Chemical Industries Ltd. and has been found to be satisfactory and reliable. However, attempts to move this equipment into the production plant with the intention of using it for fully automatic control have given rise to various difficulties: the one dealt with in this paper arises from the fact that although a flame photometer provides a simple and convenient method for the determination of potassium when used in a laboratory, its use in the plant has the following disadvantages.

1. Fertilizer dust suspended in the plant atmosphere contaminates the flame and introduces errors.
2. The presence of a naked flame is undesirable in some plant areas.
3. The continuous supply of oxygen and propane is not always convenient to arrange.

The approach to this problem described here involves the determination of potassium by mixing the fertilizer solution with excess of sodium tetraphenylborate, filtering off the potassium tetraphenylborate precipitated, and measuring the excess of reagent by its absorbance at 254 mμ.

A survey of available methods for the quantitative determination of potassium indicated that either a colorimetric or a turbidimetric procedure would be the most suitable replacement for the flame photometric method usually adopted in the Auto-Analyzer system. Many methods,[2] with a variety of reagents, have been described for the colorimetric or turbidimetric determination of potassium but, taking low

solubility of the final potassium salt as a criterion, either sodium cobaltinitrite or sodium tetraphenylborate is the most suitable. With the cobaltinitrite reagent used in the presence of silver nitrate, the precipitated potassium silver cobaltinitrite has a solubility in water of $1{\cdot}64 \times 10^{-2}$ g/l at 25° and in aqueous media is the least soluble of all the potassium salts; potassium tetraphenylborate is only slightly more soluble in water—$3{\cdot}6 \times 10^{-2}$ g/l at 25°. However, the cobaltinitrite reagent is somewhat unstable and for this reason it was decided to use sodium tetraphenylborate as reagent.

The use of sodium tetraphenylborate (STPB) to precipitate potassium is already well-established although the reaction was first described by Wittig[3] only as recently as 1949. Subsequent work[4,5,6] has shown that it can be used for the quantitative precipitation of potassium from solution and Ford[7] successfully used the reagent for the gravimetric determination of potassium in fertilizers. For fertilizer analysis, however, a more attractive procedure is to add excess of STPB and determine the excess volumetrically by titration with a quaternary ammonium salt. A method[8] based on this principle has been adopted by the Association of Official Analytical Chemists (A.O.A.C.) Washington, D.C., and recent check analyses[9] have shown that it is accurate and precise. In Europe also a similar method is being used on an increasing scale. Since there is widespread acceptance of STPB as a reagent for the determination of potassium it was concluded that the investigation should aim to develop a spectrophotometric version of the method, which could be used with the AutoAnalyzer system and might replace the flame photometric method for analysis in a works.

A spectrophotometric method for the determination of potassium has been described by Pflaum and Howick[10] but this involves redissolving the potassium tetraphenylborate precipitate in an acetonitrile–water mixture (3 + 1) and measuring the absorbance at 266 mμ. It was considered preferable, if possible, to work with the visible region of the spectrum, and a method[11] in which the solution containing potassium is treated with excess of STPB and the excess is precipitated with *p*-rosaniline, was therefore examined. The excess of *p*-rosaniline can be measured in the visible region of the spectrum. Considerable difficulty was experienced with this method and it was finally abandoned. Attempts were then made to measure the turbidity produced by the potassium tetraphenylborate precipitate but it was found impossible to control the particle size of the suspension of potassium tetraphenylborate and it was decided to measure the excess of STPB directly by taking advantage of the absorbance bands of this substance in the ultraviolet region at 250–265 mμ.

EXPERIMENTAL

Apparatus

The apparatus used is shown diagrammatically in Fig. 1. Most of the items of equipment are standard AutoAnalyzer (Technicon Instruments Corp., Research Park, Chauncey, N.Y., U.S.A.) components and only the other items required are described in detail below.

Ultrasonic bath

The equipment was supplied by Kerry's (Ultrasonics) Ltd., Warton Road, London, E.15, and consists of a bath, a transducer and a power supply. The bath, Type KB 80/1, is constructed of 18-gauge cold-rolled steel 6 in. × 4 in. × 6 in. with a working capacity of 3 pints. Power is supplied by a Kerry "Pulsatron" Ultrasonic generator type KG 80/1, 200/240 V single phase 50 c/s, with a power consumption of 100 W and an output of 160 W peak and 40 W average, at a frequency of 80 kc/s. The power is fed to a specially designed barium titanate transducer unit permanently attached beneath the floor of the bath.

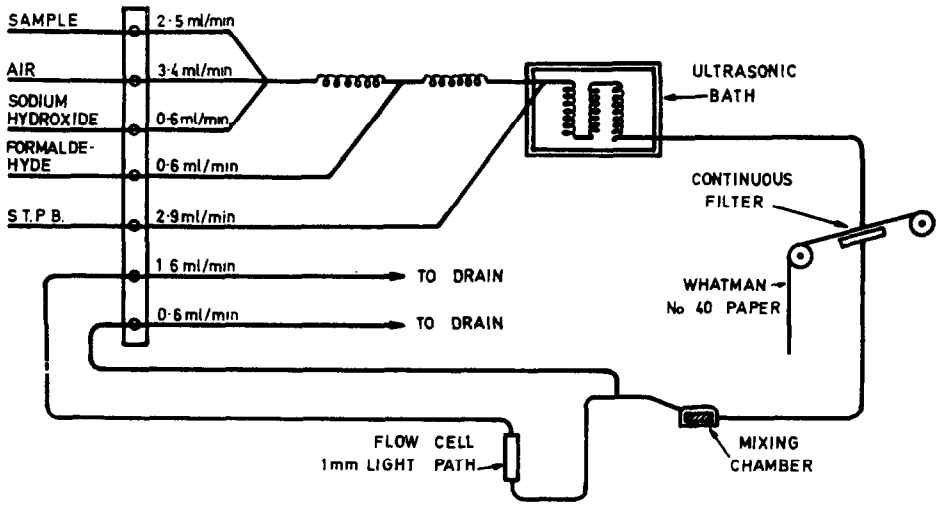

FIG. 1.—Flow system.

Filtrate mixing chamber

A drawing of the filtrate mixing chamber is shown in Fig. 2. The body of the chamber is made by sealing and flattening the end of a piece of glass tubing, 17 mm bore, and adding the inlet and outlet tubes as shown in the drawing. The outlet tube is offset to avoid trapping air bubbles. The main tubing is then cut and the ends ground level to an internal length of 8 mm. A glass disc 20 mm in diameter and 1·75 mm thick is prepared and ground flat with a 2-mm diameter depression drilled centrally to a depth slightly less than 1 mm to accommodate the spigot of the magnet follower.

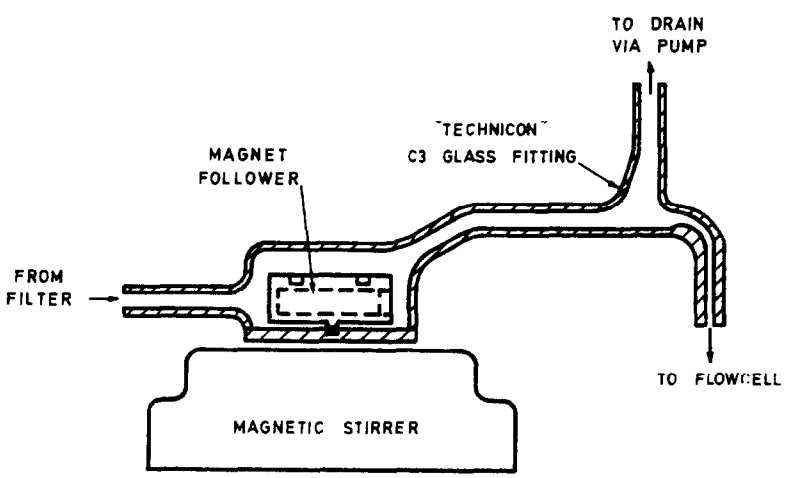

FIG. 2.—Detail of mixing chamber assembly.

The magnet follower, Fig. 3, is made from PTFE bar, 15-mm diameter, with a 5-mm diameter hole drilled through the side to a depth of 13 mm. A length of $\frac{3}{16}$ in. square cross-section "FERROBA" (Grant Instruments, Cambridge, England) is turned to just less than 5 mm in diameter, and an 11-mm length is cut and inserted into the hole, which is then sealed with a PTFE plug. The PTFE bar is then machined so that the top surface is 0·5 mm from the inner surface of the hole. Four slots 2 mm × 2 mm × 1 mm deep, set at 90° intervals, are cut on the circumference of this surface, clear of the FERROBA. The lower surface of the bar is now machined to within 0·5 mm of the inner surface of the hole but in this case a 1-mm diameter spigot 1 mm long is left to permit the correct

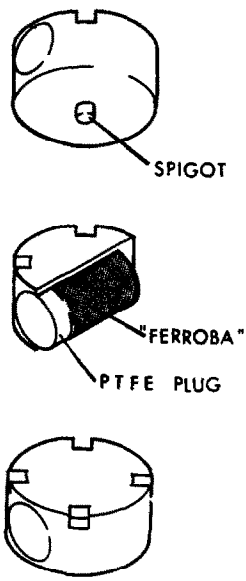

FIG. 3.—Detail of magnet follower.

positioning of the magnet follower in the base of the mixing chamber. Finally, the magnet follower is placed in the body of the chamber and the disc cemented in position with "ARALDITE" resin.

L.K.B. Uvicord ultraviolet absorptiometer

In this apparatus (L.K.B. Instruments, Inc., Washington 14, D.C., U.S.A.) ultraviolet light from a mercury vapour lamp passes through an adjustable slit. A liquid filter (nickel sulphate solution) on the other side of the slit absorbs most of the unwanted radiation at 312·6 mμ and 313·2 mμ and light which is essentially monochromatic (253·7 mμ) then passes through the measuring cell. The light is absorbed in the cell to an extent characteristic of the solution flowing through it. Unabsorbed ultraviolet light continues through a black glass filter and on to a phototube detector. The black glass filter absorbs any visible light coming from the mercury vapour lamp or from external sources. In the experiments described in this paper a quartz cell with a 1-mm optical path and volume of 0·05 ml was used.

Reagents

Formaldehyde solution 10% *w/v*. Dilute 275 ml of formaldehyde solution, analytical reagent grade 36% w/v, to 1 litre.

Sodium hydroxide solution 5% *w/v*.

Sodium tetraphenylborate solution, 0·2%. The solution may occasionally be cloudy and should be filtered through a Whatman No. 40 paper.

Procedure

Transfer the appropriate weight (1·5 g for 20% K_2O, 3·0 g for 10% K_2O) of the prepared sample (ground to pass a 0·152-mm aperture sieve) to a suitable beaker, add 200 ml of water and heat to boiling. Cover with a clock glass, continue to boil gently for 15 min, then cool and dilute with water to 1 litre in a volumetric flask. Filter sufficient solution for test through a Whatman No. 40 paper.

Set up the manifold system as shown in Fig. 1. With distilled water passing through the sample and reagent lines and with the slit fully closed, adjust the zero controls on the absorptiometric control unit until the recorder pen indicates zero transmission. The system is now ready for introduction of the reagent solutions; when a steady base line has been obtained introduce bracketing standards appropriate to the level of potassium expected, using an AutoAnalyzer Mark II sampler with a 2-min water wash and 4-min sample aspiration time. Aspirate the filtered sample solution immediately after the standards.

RESULTS AND DISCUSSION

Experiments in the visible region

As mentioned above, it was decided to concentrate initially on a spectrophotometric method in which potassium is precipitated with STPB and the excess of tetraphenylborate (TPB) ion is precipitated by the addition of excess of *p*-rosaniline. The precipitates can be filtered off and the excess of *p*-rosaniline in the filtrate measured spectrophotometrically at 525 mμ. Standard AutoAnalyzer equipment was used, comprising a sampler, pump, 2 dialysers, colorimeter and recorder.

The potassium-bearing solution was mixed with a stream of STPB reagent which precipitated potassium tetraphenylborate, and part of the excess of TPB ion was dialysed—a process which also separated the potassium precipitate. The dialysed TPB ions were then mixed with excess of *p*-rosaniline and the precipitated *p*-rosaniline TPB was removed by passage through a second dialyser. Some *p*-rosaniline dialysed into the recipient stream and the concentration was measured absorptiometrically at 525 mμ. As might have been expected, a number of difficulties were experienced with this complicated system. Foremost of these was the trouble caused by deposition of potassium TPB and *p*-rosaniline TPB on the walls of the transmission tubing. Moreover, *p*-rosaniline appeared to be absorbed into the transmission tubing and there were memory effects in the dialyser possibly due to variations in the dialysis process caused by blockage of the membrane with precipitate. Further work on this method was, therefore, abandoned.

It was next decided to ascertain whether or not a simple turbidimetric method might be possible, analogous to the standard AutoAnalyzer method for determination of sulphate. Although the investigation of this method was not exhaustive it did appear that the particle size of the precipitate was too large; with concentrated solutions the mean diameter of the potassium TPB precipitate was 20 μ and although this could be reduced by using more dilute solutions, these small crystals quickly formed aggregates of about 20 μ diameter. As a consequence of the large particle or aggregate size of the precipitate the recorder traces were very irregular. For comparison, a barium sulphate precipitate formed under conditions suitable for turbidimetric measurement was also examined, and found to have a mean particle size of 1 μ. The effect of temperature was also investigated and found to cause some slight increase in particle size. Several anticoagulants were also tried without success.

At this point it was decided to use a method in which the potassium TPB was filtered off and the concentration of the residual TPB ion was measured in the ultraviolet region of the spectrum.

Experiments in the ultraviolet region

Preliminary experiments using a solution of STPB to obtain an absorbance trace on a Unicam SP 800 indicated that the appropriate wavelength for measurement of absorption by the TPB ion was 266 mμ; this is in accord with the findings of Pflaum and Howick.[10] A typical trace is shown in Fig. 4 from which it may be seen that there are two shoulders on the absorbance curve, one at 273 mμ and one at 266 mμ. The latter was chosen since it is the more sensitive. A continuous flow system was therefore set up incorporating a standard AutoAnalyzer sampler, pump and continuous filter, followed by a Beckman DB spectrophotometer and recorder. The spectrophotometer was fitted with a flow-through cell with a small volume of about 0·2 ml,

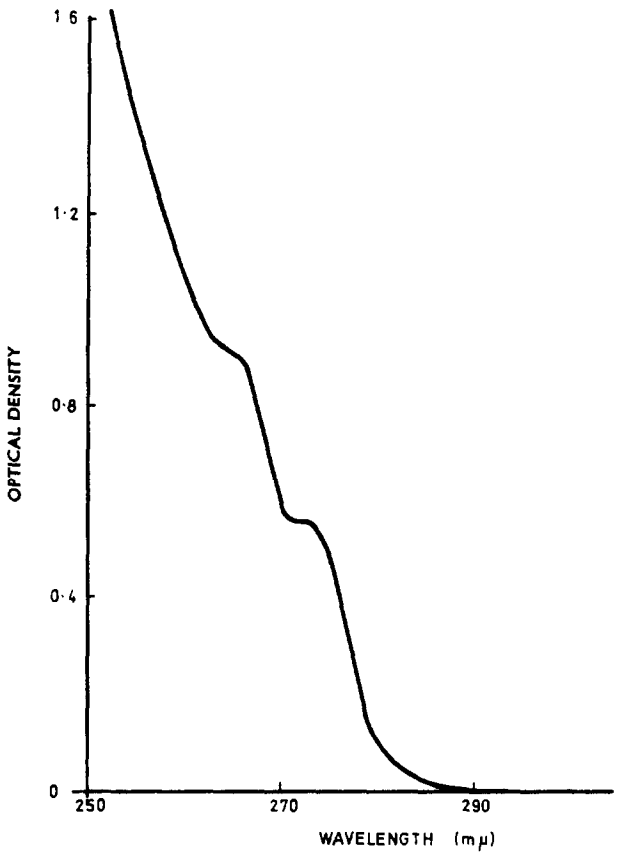

FIG. 4.—Absorption spectrum of sodium tetraphenylborate solution (0·01% w/v in water; 1-cm cuvette).

which minimized the response time of the system. It was also necessary to make provision in the manifold system for a preliminary treatment of the sample solution with 10% formaldehyde solution to destroy any ammonium ions present. After mixing with a 0·20% STPB solution the sample stream was passed through three mixing coils to ensure complete precipitation before passing to the continuous filter and thence to the spectrophotometer. A plot of absorbance against concentration gave a linear calibration graph for concentrations of K_2O up to 300 mg/l in the sample solution. At higher concentrations solubility effects caused slight deviation from linearity. The principle of the method is thus shown to be sound but it was considered preferable for routine use to employ a simple type of filter absorptiometer rather than the Beckman monochromator. An L.K.B. Uvicord absorptiometer was therefore substituted for the Beckman instrument.

Initially it was found that irregular recorder traces were obtained when using the absorptiometer and it was apparent that the principal cause of this was variations in the concentration of STPB from segment to segment in the flow system. Normally such variations are not troublesome but when the extremely small volume (0·05 ml) flow-cell in the Uvicord absorptiometer is used the effect is magnified and must be

eliminated. This was achieved by inserting a small reservoir (about 2 ml in volume) in the system to collect the filtrate from the continuous filter. A small magnetic stirrer was also included to ensure thorough mixing of the filtrate. For the correct functioning of the chamber, it was necessary to make provision for a de-bubbling step on the outlet line to prevent air bubbles, which occasionally pass through the filter, from being drawn through the flow-cell.

This manifold system gave excellent results when tested with standard fertilizer samples but could not be operated for more than about 4 hr owing to the build-up of precipitate in the mixing coils. It thus became necessary to immerse these coils in the ultrasonic bath shown in the manifold diagram. This was actuated by a timing mechanism which enabled the precipitate to be removed by switching on the generator for 1 min every hour. No further difficulty was experienced with this system.

A series of samples was examined, using as standards fertilizer samples analysed by the potassium chloroplatinate method described in the Fertilisers and Feeding Stuffs Regulations 1960, Section 5.2, Statutory Instrument 1165 published by Her Majesty's Stationery Office, London. Simultaneously, the same samples were analysed for potassium with a Technicon AutoAnalyzer flame photometer; in this instance also the bracketing standards used were analysed by the potassium chloroplatinate method previously mentioned. The results obtained by both techniques are given in Table I.

Both sets of results are the average of 3 independent determinations on each sample and it can be seen that the results are in close agreement. Statistical analysis of the individual determinations by the *F*-test indicated that there is a significant difference in the precision of the two procedures, the STPB method being more precise than the flame photometer method. Application of the *t*-test gave no evidence of a bias between the two methods. These results clearly indicate that this automatic absorptiometric procedure is capable of giving acceptable results for the determination of potash in fertilizers. Certain anomalies were observed from time to time with respect to the nature of the precipitated potassium TPB, which varied from a granular crystalline precipitate to a finely divided suspension. Various authors[5,6,12,13,14] have discussed the optimum conditions for the precipitation of potassium TPB but it was impractical to apply their findings to a continuous system. Moreover, the form of the precipitate did not affect the results obtained so it was considered unnecessary to investigate this aspect any further. If required, the sodium tetraphenylborate reagent may be purified, since there is evidence that trace impurities can affect the absorbance of the solution, but here again the results are not invalidated, the effect being merely to alter the absolute value of the absorbance and the slope of the calibration curve.

An automatic absorptiometric method for the determination of potassium in fertilizers has been developed which gives results at least as reliable as those obtained by standard procedures. The method is free from most of the disadvantages of the flame photometric method, and is generally applicable to the determination of potassium.

Using the manifold and flow system described above, the annual running cost in the U.K. for chemicals only, on a 24-hr, 350-day basis is £820. The main item in these costs is the price of the STPB and any significant reduction in this resulting from using a commercial grade would reduce the cost of operating the system by an almost proportionate amount. For comparison on the same basis, the continuous

TABLE I.—COMPARISON OF RESULTS OF DETERMINATION OF POTASSIUM IN VARIOUS FERTILIZERS BY FLAME PHOTOMETRIC AND ABSORPTIOMETRIC PROCEDURES

Type no.	Sample no.	K_2O, %	
		Flame photometric	Absorptiometric
1	1	19·0	19·0
	2	20·6	20·6
	3	21·0	20·9
	4	20·5	20·6
	5	21·1	21·1
	6	20·9	21·0
	7	21·6	22·0
	8	20·0	20·0
2	1	10·5	10·4
	2	10·2	10·1
	3	10·5	10·5
	4	10·7	10·6
	5	10·6	10·6
	6	10·5	10·4
	7	11·5	11·6
3	1	16·8	16·9
	2	18·5	18·6
	3	18·0	18·1
	4	17·7	17·7
4	1	15·3	15·2
	2	13·3	13·3
	3	13·2	13·1
5	1	19·8	19·8
	2	20·3	20·3
	3	20·4	20·4
6	1	20·8	21·0
	2	20·8	20·9
	3	20·9	20·9
7	1	9·5	9·5
	2	10·1	10·1
	3	10·2	10·1
8	1	16·5	16·3
	2	21·1	21·3
9		9·0	8·9
10		11·8	11·5
11		12·8	12·7
12		15·9	15·9
13		17·3	17·2
14		23·1	23·5
15		20·4	20·5

operation of the flame photometer for the determination of potassium costs about £420 per annum for the oxygen and propane gases alone. The absorptiometric method is therefore more expensive to run and in one year the extra cost totals approximately £400. However, the advantages attendant on its use far outweigh the disadvantage of increased cost.

This work has shown that a reliable continuous method for the determination of potassium can be obtained based on the ultraviolet spectrophotometry of tetraphenylborate solutions. It is of interest to note that some years ago Cooper[15] claimed

to have developed a satisfactory laboratory procedure for the quantitative determination of potassium ion, based on this principle, but gave no details. The automatic method described in this paper can also be used manually and under standard laboratory conditions has given excellent results.

Acknowledgements—This work extended over a period of two years and during this time several people made valuable contributions, but we are especially indebted to Mr. S. G. Farrow and Mr. S. R. Hill whose assistance enabled us to bring the work to a successful conclusion.

Zusammenfassung—Ein automatisches Verfahren zur Bestimmung von Kalium durch UV-Absorptionsmessung wurde entwickelt. Dabei wird Kalium durch Zugabe eines bekannten Überschusses von Natriumtetraphenyloborat gefällt, der Niederschlag von Kaliumtetraphenyloborat durch Filtration entfernt und der Überschuß von Natriumtetraphenyloborat im Filtrat über seine Absorption bei 254 nm gemessen. Der größte Teil der Apparatur, darunter auch ein kontinuierlich arbeitendes Filter, ist normales AutoAnalyzer-Gerät; das übliche Kolorimeter wird jedoch durch ein Uvicord-Absorptiometer ersetzt. Ein Ausfallen von Niederschlag im System wird verhindert, indem die Misch-Schlangen in ein Ultraschallbad getaucht werden, das von Zeit zu Zeit durch einen einfachen Zeitgebermechanismus in Betrieb gesetzt wird. Die Methode eignet sich zur Kaliumbestimmung im Produktionsbetrieb, wo Ergebnisse vom Flammenphotometer zuweilen durch Düngemittelstaub in der Luft um den Brenner beeinträchtigt werden.

Résumé—On a élaboré une méthode absorptionmétrique ultraviolette automatique pour le dosage du potassium. La méthode comprend une précipitation du potassium par addition d'un excès connu de tétraphénylborate de sodium, l'élimination du précipité de tétraphénylborate de potassium par filtration et la mesure de l'excès de tétraphénylborate de sodium dans le filtrat au moyen de son absorption à 254 mμ. La majeure partie de l'appareil, comprenant un filtre continu, est l'équipment standard AutoAnalyzer, mais un absorptionmètre ultraviolet Uvicord remplace le colorimètre habituel. On élimine l'établissement de précipité dans le système en immergeant les serpentins de mélange dans un bain ultrasonique qui est actionné de façon intermittente par un simple mécanisme de minuterie. La méthode convient spécialement à l'analyse du potassium dans une plante industrielle où les résultats du spectrophotomètre de flamme sont parfois affectés par le poussière d'engrais dans l'air entourant le brûleur.

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APPLICATION OF THE ZONE MELTING TECHNIQUE TO METAL CHELATE SYSTEMS—II*

CONCENTRATION OF A TRACE AMOUNT OF METAL ACETYLACETONATE IN CHROMIUM(III) ACETYLACETONATE†

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Summary—The zone melting process was applied to tris(acetylacetonato)chromium(III) which contained a trace amount of aluminium(III), iron(III), copper(II), manganese(III), nickel(II) cobalt(III) and rhodium(III) in the forms of their acetylacetonates, and the highly purified chromium chelate was found in the top portion of a column, while the minor components except the rhodium chelate were concentrated in the bottom portion. The rhodium chelate was concentrated in the top portion. Ease of migration of the minor components during the zone melting process decreased in the order Cu, Fe, Mn, Co, Ni, Al and Rh, and was accounted for in terms of their crystal structures. Extremely slow speed of zone travel caused an increase of the distribution coefficient; this was due to back diffusion of minor components into a congealed solid phase from a molten zone.

WE have been successful in applying the zone melting technique to systems containing metal chelates.[1,2] Results were previously reported for a system consisting of tris(acetylacetonato)chromium(III) (main component) and tris(acetylacetonato)aluminium(III) (minor component).[3] The distribution coefficient (k) of the aluminium chelate in the chromium chelate was examined and was found to reach a minimum value at a certain speed of zone travel, and to increase towards unity for faster and slower speeds. This phenomenon was presumed to be due to back-diffusion of the minor component into a congealed solid from a molten zone. Experimental proof that the presumption was correct is shown in the present paper.

This paper is also concerned with an investigation on the behaviour of various metal acetylacetonates in tris(acetylacetonato)chromium(III) during the zone melting process. The results suggest that the acetylacetonate from crude chromium(III) salts could be highly purified from impurities such as iron(III), copper(III), manganese(III), cobalt(III), aluminium(III), nickel(II) and rhodium(III) acetylacetonates, and these impurities could be concentrated and separated.

In the course of the study, phase diagrams were constructed for the tris(acetylacetonato)aluminium(III)–tris(acetylacetonato)chromium(III) and tris(acetylacetonato)rhodium(III)–tris(acetylacetonato)chromium(III) systems, in order to

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establish the relationship between the phase diagram and the distribution coefficient, since these two systems represent the cases where the distribution coefficients are smaller and larger than unity respectively.

EXPERIMENTAL

Reagents

Metal acetylacetonates, prepared by standard procedures,[4] were purified by repeated recrystallization. Their melting points and analytical results are summarized in Table I.

TABLE I.—PROPERTIES OF METAL CHELATES

Chelate*	m.p., °C	Analyses Found, %	Calc., %
$Cr(AA)_3$	216·1 – 18·3	C, 51·4	C, 51·58
		H, 6·1	H, 6·06
$Al(AA)_3$	195·0 – 95·4	C, 55·6	C, 55·55
		H, 6·6	H, 6·53
$Fe(AA)_3$	178·0 – 78·5	Fe, 15·42	Fe, 15·81
$Mn(AA)_3$	290 (decomp.)	Mn, 15·65	Mn, 16·60
$Cu(AA)_2$	230 (decomp.)	Cu, 24·55	Cu, 24·27
$Co(AA)_3$	213 (decomp.)	Co, 16·49	Co, 16·54
$Ni(AA)_2$	228 (decomp.)	Ni, 22·86	Ni, 22·85
$Rh(AA)_3$	259·7 – 60·6	C, 44·4	C, 45·02
		H, 5·3	H, 5·29

* AA stands for a univalent acetylacetonate ion.

Procedure

The general procedure is that given previously.[3] Aluminium(III), iron(III), manganese(III), copper(II), cobalt(III) and nickel(II) in chromium(III) were determined by emission spectrography. Analytical line pairs selected for the determination of the metals are shown in Table II.

TABLE II.—LINE PAIRS FOR EMISSION SPECTROGRAPHIC ANALYSIS

Metal ion	Line pair, Å	
Al	Al 3082·155	Cr 3084·56
Fe	Fe 2599·396	Cr 2603·570
Mn	Mn 2593·729	Cr 2596·173
Cu	Cu 3273·962	Cr 3264·264
Co	Co 3412·339	Cr 3411·080
Ni	Ni 3002·491	Cr 3011·09

Rhodium(III) was determined by atomic absorption spectrophotometry on the rhodium absorption line at 3435 Å. The instrument was a Jarrel-Ash Model AA-1 and the solvent was a mixture of methanol and benzene (1:1).

Diffusion experiments

Tris(acetylacetonato)aluminium(III) was packed tightly on a column of tris(acetylacetonato)-chromium(III) which was cast into a teflon tube (9 mm inner diameter). The tube was stoppered at both ends with glass plugs and inverted, then heated at a temperature below the melting points of both components (166°). It was then cut into pieces 2 mm long and a sample from each piece was analysed for aluminium by emission spectrography.

Phase diagrams

The melting points of binary mixtures of various compositions were determined by differential thermal analysis.

RESULTS AND DISCUSSION

The distribution coefficient was found to increase towards unity when the speed of zone travel was too slow, and this phenomenon was due to back-diffusion of the minor component into the solid matrix from the melt. The diffusion experiment with aluminium(III) and chromium(III) acetylacetonates in contact at a boundary plane showed that the aluminium chelate migrated into the chromium chelate as far as 10 mm from the boundary plane at 166° (Fig. 1), at which temperature the whole system was solid over the entire range of composition (Fig. 2). The result seemed to be

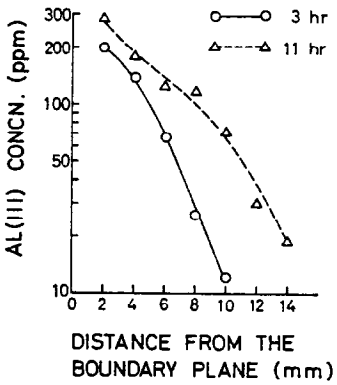

FIG. 1.—Diffusion of $Al(AA)_3$ in solid $Cr(AA)_3$ when heated at 166°C for 3 hr and 11 hr respectively.

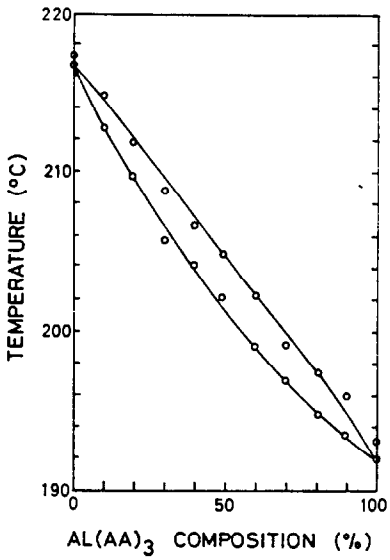

FIG. 2.—Phase diagram of the binary system $Al(AA)_3$–$Cr(AA)_3$.

indicative of the diffusion of the aluminium chelate through the solid chromium chelate. When a zone travels at an extremely slow speed, the neighbourhood of a boundary plane between a congealed solid and a molten zone will be subjected to a temperature just below the melting point for a considerable period of time. Under these conditions, the impurities in the molten zone may diffuse back into the congealed solid.

In addition to back-diffusion, the crystals in their melt, when cooled very slowly, tend to grow arborescently and become intertwined holding the melt, which solidifies as an inclusion. This causes less effective separation and hence an increased distribution coefficient.

Figures 3–8 show the results of the zone melting experiments on the binary systems with the chromium(III) chelate as the main component. The concentration of the minor component is plotted against the distance in zone lengths, x/l, where x is the distance from the top to the point where the sample was cut out for the determination, and l is the length of the molten zone.

As shown in Figs. 3 and 4, iron(III) and and copper(II) chelates are so easily concentrated at the bottom of the column that their concentrations in the top portion

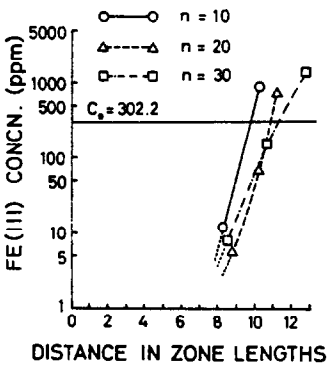

FIG. 3.—Distribution of $Fe(AA)_3$ in $Cr(AA)_3$ after zone melting.
C_0—Initial concentration of the metal ion
n—Number of the passages of a molten zone.

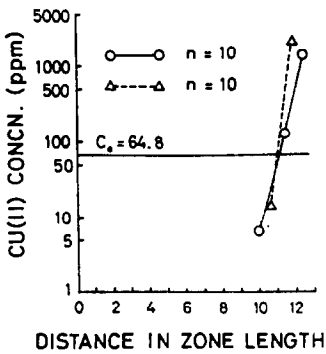

FIG. 4.—Distribution of $Cu(AA)_2$ in $Cr(AA)_3$ after zone melting.

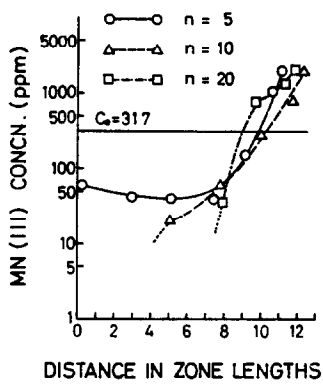

FIG. 5.—Distribution of $Mn(AA)_3$ in $Cr(AA)_3$ after zone melting.

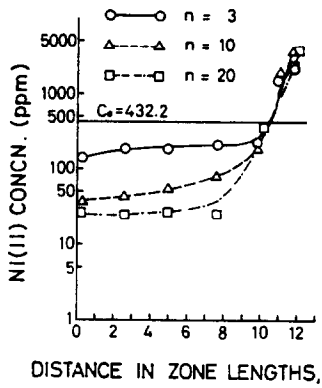

FIG. 6.—Distribution of $Ni(AA)_2$ in $Cr(AA)_3$ after zone melting.

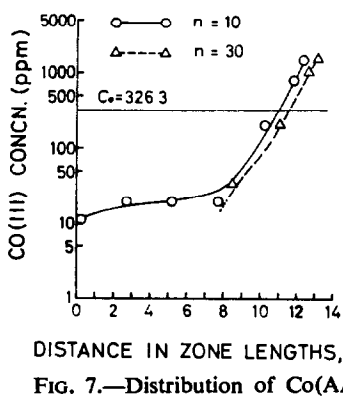

FIG. 7.—Distribution of $Co(AA)_3$ in $Cr(AA)_3$ after zone melting.

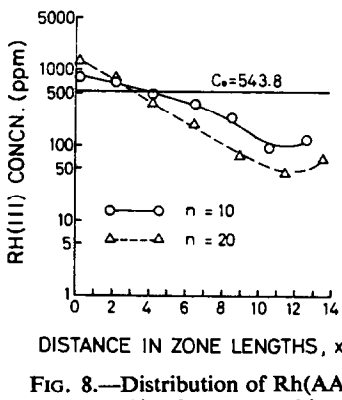

FIG. 8.—Distribution of $Rh(AA)_3$ in $Cr(AA)_3$ after zone melting.

are reduced far below the analytical sensitivities of the instruments, after only 10 passages.

In the determination of the distribution coefficients of the iron and copper chelates in the chromium chelate, the larger part of each had migrated to the bottom portion after a single passage of a molten zone at a speed of 15, 27 or 40 mm/hr. Since the Sorensen[5] method could therefore not be applied, the distribution coefficients were determined, for the last case only, by Sue's method.[6] The approximate values were 0·37 and 0·43 for copper and iron respectively.

Study of the binary systems indicates that the chelates of aluminium, nickel, manganese and cobalt were all concentrated at the bottom, but the concentration effect was poor for aluminium and intermediate for the rest. In contrast, the rhodium chelate was concentrated at the top of the column, indicating that the distribution coefficient is higher than unity, and this was proved by examination of the phase diagram of the system (Fig. 9).

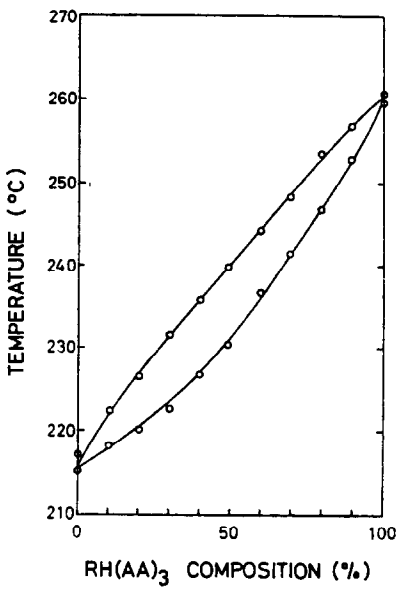

FIG. 9.—Phase diagram of the binary system $Rh(AA)_3$–$Cr(AA)_3$.

It is likely that the crystal structure of the metal chelates plays an important role in the difference in their mobilities in the matrix during the zone melting process. The trisacetylacetonates of chromium(III), aluminium(III), manganese(III), cobalt(III) and rhodium(III) are known to form a monoclinic isomorphic set, with a similar size of unit cell and the same space group C_{2h}^5,[7] whereas the iron(III)[8] and copper(II)[9] chelates are orthorhombic and monoclinic respectively and their cell dimensions are different from those of the chromium chelate.

The binary systems of aluminium(III) and chromium(III) chelates (Fig. 2) and of rhodium(III) and chromium(III) chelates (Fig. 9) each form a complete solution in both solid and liquid phase over the entire range of composition; aluminium and

rhodium chelates, therefore, seem to be more soluble in the solid chromium chelate than the rest. Formation of complete solid solution of any composition is encountered very often in systems of components having similarities in crystal structure as well as in molecular structure.

Thus, it is likely that metal chelates with different crystal structures segregate more easily than those with similar ones.

To investigate mutual interaction among the minor components present, multi-component systems (aluminium(III), copper(II) and iron(III) chelates in the chromium chelate; aluminium(III), manganese(III) and cobalt(III) chelates in the chromium chelate) were studied. The first system consists of chelates of different crystal structures, and the second of chelates forming a monoclinic isomorphic set. Their distribution in the chromium chelate is shown in Figs. 10 and 11, indicating that the

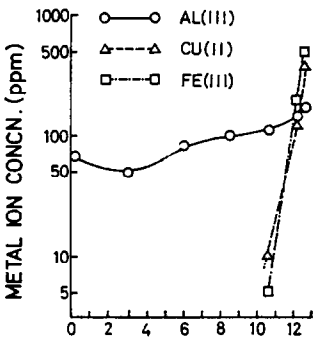

FIG. 10.—Distribution of the metal acetylacetonate chelates in $Cr(AA)_3$ after zone melting.
$n = 10$; C_0 for Al, Cu and Fe is 85·2, 25·6 and 29·1 ppm respectively.

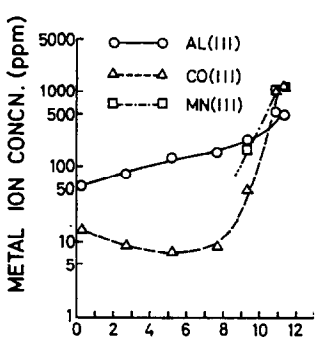

FIG. 11.—Distribution of the metal acetylacetonates in $Cr(AA)_3$ after zone melting.
$n = 20$; C_0 for Al, Co and Mn is 157·2, 157·5 and 150·5 ppm respectively

efficiency of concentrating each component is nearly equal to that for each binary system, and that there is no interaction.

Our results afforded an experimental foundation for the possibility of zone refining purification of acetylacetonates obtained from crude chromium salts. The zone refining of metallic chromium is known to be difficult because of its high volatility at the melting point, so this new process seems to be a useful method of obtaining highly purified chromium compounds. It also promises to be a useful method for the preconcentration of trace foreign components in a metal chelate.

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Zusammenfassung—Das Zonenschmelzverfahren wurde auf Tris-acetylacetonatochrom(III) angewandt, das Spurenmengen Aluminium (III), Eisen(III), Kupfer(II), Mangan(III), Nickel(II), Kobalt(III) und Rhodium(III) in Form ihrer Acetylacetonate enthielt; das hochgereinigte Chromchelat fand sich im oberen Teil der Säule, während die

Nebenbestandteile außer dem Rhodiumchelat im unteren Teil angereichert waren. Das Rhodiumchelat war im oberen Teil angereichert. Die Leichtigkeit der Wanderung der Nebenbestandteile während des Zonenschmelzprozesses nahm ab in der Reihenfolge Cu, Fe, Mn, Co, Ni, Al und Rh; dieser Gang wird mit den Kristallstrukturen erklärt. Extrem langsame Zonenverschiebung ließ den Verteilungskoeffizienten ansteigen; dies rührt von der Rückdiffusion von Nebenbestandteilen aus einer geschmolzenen in eine wieder erstarrte Zone.

Résumé—On a appliqué la méthode par fusion de zone au tris (acétylacétonato)chrome(III))contenant des traces d'aluminium(III), fer(III), cuivre(II), manganèse(III), nickel(II), cobalt(III) et rhodium(III) sous forme de leurs acétylacétonates et l'on a trouvé le chélate de chrome hautement purifié dans la partie supérieure d'une colonne, alors que les constituants mineurs à l'exception du chélate de rhodium ont été concentrés dans la partie inférieure. Le chélate de rhodium a été concentré dans la partie supérieure. La facilité de migration des constituants mineurs durant le processus de fusion de zone décroît dans l'ordre Cu, Fe, Mn, Co, Ni, Al et Rh et a été interprétée en fonction de leur structure cristalline. Une vitesse extrêmement faible du cheminement de la zone a causé un accorissement du coefficient de distribution; ceci était dû à une diffusion en retour des constituants mineurs dans une phase solide congelée à partir d'une zone fondue.

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APPLICATION OF THE ZONE MELTING TECHNIQUE TO METAL CHELATE SYSTEMS—IV*

CONCENTRATION OF METAL-8-HYDROXYQUINOLINE CHELATES IN 8-HYDROXYQUINOLINE

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Summary—The zone melting technique has been applied to 8-hydroxyquinoline containing trace amounts of various metal 8-hydroxyquinolates such as the nickel(II), cobalt(II), zinc(II) and copper(II) chelates. The metal chelate in each system was concentrated in the direction of zone travel. The highest concentrating effect was observed in the copper(II) chelate system. The concentration ratio, defined as the fraction of the metal chelate concentrated in the bottom 15% of the column, was determined after the 30th passage. A trace amount of copper ion extracted with a large excess of 8-hydroxyquinoline, was concentrated by means of the zone melting technique. The concentration ratio was 96%.

THE zone melting technique has been applied to the purification of metals and compounds. Modifications of the method have been employed to obtain a mixture of uniform composition. On the same basis, this method is applicable to concentration of trace impurities.

We have been successful in applying a zone melting technique to systems containing metal chelates. Characteristics of the technique were discussed in a previous paper.[1]

Our preliminary investigation[2] on the system of a free ligand containing trace amounts of its metal chelates, showed that trace metal ions could be concentrated at one end of the column. Thus, a zone melting process could be useful for the concentration of trace metal ions which were extracted in the form of metal chelates together with a large excess of the free ligand.

In these systems, the ligand must melt at a lower temperature than the chelates and solidify easily at its melting point (under forced cooling, if necessary). The metal chelates need not be stable at higher temperatures because the samples are processed near the melting point of the ligand, which is generally much lower than the decomposition temperatures of the chelates. The melting point of the free ligand should be low enough for the metal chelate to dissolve without thermal decomposition, but not so low that forced cooling is necessary as this may cause peritectism, and less effective separation.

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The present paper is concerned with a detailed investigation on the binary systems of 8-hydroxyquinoline (oxine) with its nickel(II), cobalt(II), zinc(II), copper(II) and iron(III) chelates. In order to discuss the effectiveness of concentrating a minor component, we have introduced a quantitative measure "concentration ratio". This value is the fraction of the minor component concentrated in the bottom 15% of the total column length.

In most analytical procedures, a large excess of chelating agent need not be used for the extraction of metal ions in an aqueous solution. However, when the extraction has to be carried out under very mild conditions without destroying the matrix material, then the samples may have to be extracted repeatedly with a large excess of chelating agent. Zone melting concentration procedures may then be useful for isolating the metal chelates.

EXPERIMENTAL

Materials

The 8-hydroxyquinoline (analytical grade) was purified by distillation, and the metal chelates, which were prepared by standard procedures, were purified by washing with hot water. Analyses of these materials were satisfactory.

Found: Zn, 18·44; $Zn(C_9H_6NO)_2$ requires Zn, 18·49%.
Found: Cu, 18·11; $Cu(C_9H_6NO)_2$ requires Cu, 18·06%.
Found: Ni, 16·85; $Ni(C_9H_6NO)_2$ requires Ni, 16·92%.
Found: Co, 16·90; $Co(C_9H_6NO)_2$ requires Co, 16·97%.

Apparatus and procedures

The apparatus consisted of devices pulling upwards 8 glass tubes simultaneously at a speed of 28 mm/hr, with a two-stage nichrome heater for each glass tube; the tubes were 4 mm bore and each contained 2·50 g of sample.

Determination of metal ions. After the requisite number of passages, the sample column was cut into pieces 20–25 mm long. The sample from each piece was weighed and then dissolved in chloroform, and the amount of metal chelate was determined spectrophotometrically against a reagent blank. The absorption maxima of $Cu(Ox)_2$, $Zn(Ox)_2$, $Ni(Ox)_2$ and $Co(Ox)_2$ in chloroform were 410, 380, 380 and 420 mμ respectively. Amounts of copper lower than the photometric determination range were determined by atomic absorption spectrophotometry with a Jarrel-Ash Model AA-1 instrument.

Preparation of test sample and model extraction of copper ion. The 8-hydroxyquinoline solution was prepared by dissolving 2·7 g of 8-hydroxyquinoline in 7 ml of glacial acetic acid, then diluting with demineralized water to 100 ml. A 5-ml aliquot of copper acetate solution containing 2·397 μg of copper/ml, was treated with 5 ml of the 8-hydroxyquinoline solution at pH 3–4 (ammonium acetate buffer). The precipitate was extracted with chloroform. The aqueous layer was again treated with the rest of the 8-hydroxyquinoline solution at pH 7 (ammonia buffer). The precipitate was extracted with another lot of chloroform. The chloroform solutions were combined, dried over sodium sulphate, and evaporated to dryness. The residual solid was subjected to the zone melting process. After the 30th zone passage, a test piece 30 mm long, cut out of the column at the bottom, was dissolved in isobutyl methyl ketone and the amount of copper ion was determined by atomic absorption spectrophotometry at 3247 Å.

RESULTS AND DISCUSSION

The distributions of the metal ions after the zone melting process are shown in Figs. 1–4. The metal concentration is plotted against the distance in zone lengths, x/l, where x is the distance from the top to the point at which the sample was cut out for the determination, and l is the length of the molten zone. The chelate in every system was concentrated at the bottom. The concentrating effect decreased in the order Cu, Zn, Fe, Co and Ni. For the copper(II) system, an average of 30·7 μg of the 31·8 μg of copper taken was found to be concentrated in the bottom 15% of the column. The concentration ratio of 97% had a relative standard deviation of 2% (8 runs) and was in a good agreement with the calculated value (Table I).

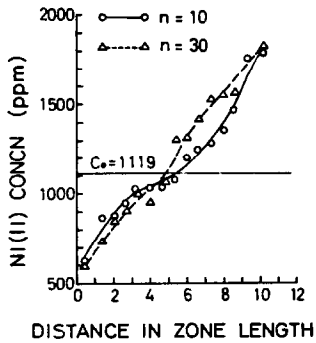

FIG. 1.—Distribution of metal ion concentration after zone melting the system bis(8-hydroxyquinolino)nickel(II) and 8-hydroxyquinoline.
C_0—initial concentration of the metal ion;
n—number of passages of molten zone.

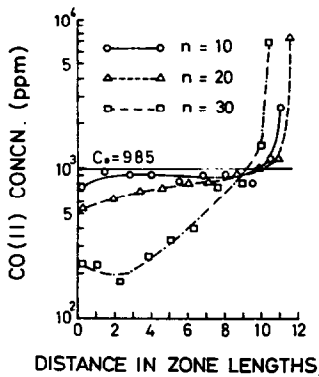

FIG. 2.—Distribution of metal ion concentration after zone melting the system bis(8-hydroxyquinolino)cobalt(II) and 8-hydroxyquinoline.

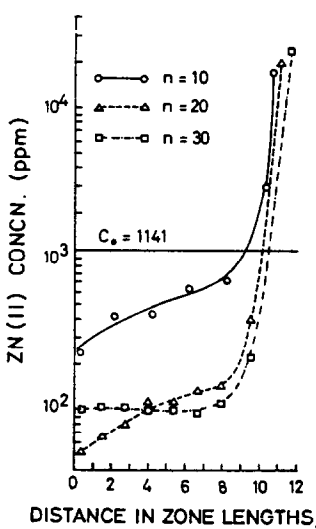

FIG. 3.—Distribution of metal ion concentration after zone melting the system bis(8-hydroxyquinolino)zinc(II) and 8-hydroxyquinoline.

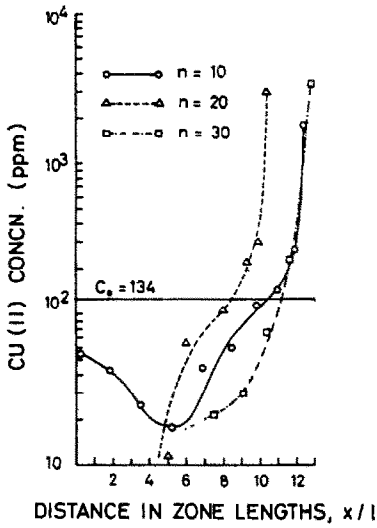

FIG. 4.—Distribution of metal ion concentration after zone melting the system of bis(8-hydroxyquinolino)copper(II) and 8-hydroxyquinoline.

TABLE I.—COMPARISONS OF THE CONCENTRATION RATIO AFTER THE 30TH ZONE PASSAGE

l/L	Concentration ratio, %		
	Calc.		Found
	$k = 0{\cdot}40$	$k = 0{\cdot}50$	$k = 0{\cdot}45$*
0·07	97·3	93·0	
0·08	96·3	91·5	96·6†
0·09	94·7	89·7	

k—distribution coefficient.
l—length of the molten zone.
L—total length of the column.

* Estimated by Sorensen's method.[8]
† The l/L value in the experimental work was nearly 0·08.

TABLE II.—EFFECT OF SPEED OF ZONE TRAVEL ON THE CONCENTRATION RATIO

Speed of zone travel, *mm/hr*	No. of zone passes	Concn. ratio
5·4	10	76·6%
15	10	88·5
15	20	89·5
28	30	96·6
40	30	60·2

The speed of zone travel affected the concentration ratio. The experimental results are summarized in Table II.

For efficiency of concentration of trace metal ions, the highest concentration ratio in the shortest time is desirable, and a zone travelling speed of 28 mm/hr was optimum for the conditions investigated.

The results of the model experiments on the extraction of copper with 8-hydroxyquinoline and the subsequent concentration of the extract by zone melting are summarized in Table III.

TABLE III.—COMPARISONS OF CONCENTRATION RATIOS OF COPPER ION AFTER ZONE MELTING

No. of zone passes	No. of runs	Average amount of Cu(II) in the bottom 15 % region, μg	Concn. ratios, %
30	3	11·0	91
40	3	11·5	96

Zone length about 15 mm; initial amount of Cu(II) in the sample solution, 12·0 μg.

After the zone melting process, the lower two thirds of the column was still yellow. The concentration ratio, however, was not affected, being satisfactorily high and in good agreement with the results described in Table I in spite of the different experimental conditions.

Acknowledgement—The authors wish to thank the Ministry of Education, Japanese Government, for financial support of this work.

Zusammenfassung—Das Zonenschmelzverfahren wurde auf 8-Hydroxychinolin angewandt, das Spuren verschiedener Metall-8-hydroxychinolate, wie z.B. die Chelate von Nickel(II), Kobalt(II), Zink(II) und Kupfer(II), enthielt. Das Metallchelat wurde in jedem System in Richtung der Zonenwanderung angereichert. Der höchste Anreicherungseffekt wurde beim Kupfer(II)-chelatsystem gefunden. Das Konzentrationsverhältnis, definiert als der Bruchteil an Metallchelat, der in den unteren 15% der Säule angereichert wird, wurde nach dem 30. Durchgang bestimmt. Eine mit einem großen Uberschuß an 8-Hydroxychinolin extrahierte Spurenmenge Kupfer wurde mit dem Zonenschmelzverfahren angereichert. Das Konzentrationsverhältnis war 96%.

Résumé—La technique de fusion de zone a été appliquée à la 8-hydroxyquinoléine contenant des traces de 8-hydroxyquinoléinates de divers métaux tels que les chélates de nickel(II), cobalt(II), aine(II) et cuivre(II). Dans chaque système, le chélate métallique a été concentré dans la direction du déplacement de la zone. L'effet de concentration le plus élevé a été observé dans le système chélate cuivre(II). Le rapport de concentration, défini par la fraction de chélate métallique concentrée dans les 15% inférieurs de la colonne, a été déterminé après le 30e passage. Une trace d'ion cuivre extraite avec un grand excès de 8-hydroxyquinoléine a été concentrée par la technique de fusion de zone. Le rapport de concentration a été de 96%.

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APPLICATION OF UREASE FOR THE PRECIPITATION OF NICKEL DIMETHYLGLYOXIMATE BY UREA FROM HOMOGENEOUS SOLUTION

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Summary—Urease can be used to decompose urea for the precipitation of nickel dimethylglyoximate from homogeneous solution. Optimum experimental conditions, and a procedure giving good separations from other ions, are described.

PRECIPITATION of nickel dimethylglyoximate from homogeneous solution was developed by Bickerdike and Willard[1] in 1952, and further, by Salesin, Abrahamson and Gordon[2] in 1962. The former utilized the pH change produced by hydrolysis of urea, and the latter the formation of dimethylglyoxime by the reaction of hydroxylamine and biacetyl.

Precipitation from homogeneous solution (PFHS) has been used widely since then as an effective means for improving the separation of ions. There are, however, still some difficulties associated with the method; for example, urea is decomposed so rapidly when heated that the pH of the solution is raised too fast and an incomplete separation of the ions results. This paper concerns a proposal[3] to use urease to decompose urea, and thus to control the pH of the solution. Experimental conditions are examined in order to achieve optimum conditions for smooth and steady precipitation from homogeneous solution.

EXPERIMENTAL

Reagents

Stock nickel solution. A 0·05*M* nickel solution was prepared by dissolving 10·00 g of nickel in 6*M* hydrochloric acid. A standard solution containing 2·5 mg of nickel per ml was prepared by further dilution.

Dimethylglyoxime, 1% ethanolic solution.

Urease, 0·01% aqueous solution prepared just before use.

Citric acid, 20% aqueous solution.

All chemicals used, except the nickel, were analytical-reagent grade.

Procedure

Transfer a known volume of nickel solution to a wide-necked 250-ml bottle, add 5 ml of citric acid solution and 50 ml of urea solution, and dilute to about 200 ml. Adjust the pH to 4·4 with ammonia solution, add 15 ml of dimethylglyoxime solution and 20 ml of urease solution, dilute to about 250 ml, stopper, and keep at 35°. Collect the nickel dimethylglyoximate by filtration on a porosity-4 sintered glass crucible, dry at 120°, cool and weigh.

RESULTS AND DISCUSSION

It was hoped that the use of urease to bring about the change in pH of the solution would enable good separations of nickel from other ions to be obtained by PFHS without heating. However, as the activity of enzymes is inhibited by the presence

of metal ions, the optimum conditions had to be established for the decomposition of urea to be carried out smoothly in the presence of nickel ions.

Urease activity

Nickel (25 mg) was found to have no measurable effect on the activity of urease for the hydrolysis of urea.

Effect of citric acid concentration

The addition of citric acid as a buffering and complexing agent is recommended for the precipitation of nickel from homogeneous solution. However, if a large amount is added, the buffering effect is too strong and the pH change is not sufficient to allow precipitation to take place. On the other hand, when insufficient is added, the pH change of the solution is not controlled smoothly, and nickel dimethylglyoximate precipitates too rapidly.

As seen in Table I, from 3 to 7 ml of a 20% citric acid solution are sufficient for satisfactory recovery of the nickel.

TABLE I.—EFFECT OF CITRIC ACID CONCENTRATION

20% citric acid added, *ml*	Nickel		Difference, *mg*
	taken, *mg*	found, *mg*	
1*	25·00	24·91	−0·09
2*	25·00	24·96	−0·04
3	25·00	24·96	−0·04
5	25·00	24·99	−0·01
7	25·00	24·90	−0·10
10	25·00	10·67	−14·37

* Precipitate appears rapidly.
Urea: 10 g, initial pH 4·4, dimethylglyoxime 15 ml, urease 20 ml, temperature 35°C, time 13–15 hr.

Effect of initial pH

The activity of urease is greatest at 35–40°, and decreases rapidly with increasing acidity of the solution. As the precipitation of nickel dimethylglyoximate is influenced by the presence of other ions, the exact pH of initial precipitation cannot be exactly stated, but precipitation usually begins at about pH 5·3 and is complete by about pH 7·1. Hence initial conditions are required under which nickel ions will remain in solution, and yet the urease will retain its activity and cause precipitation to take place.

Figure 1 shows the results of an experiment from which it can be seen that the activity of urease is inhibited in a solution with an initial pH of 4·1, the pH remaining almost unchanged for 15 hr, whereas in a solution starting at pH 4·5, slow decomposition of the urea by urease is indicated by the gradual increase in pH.

When urease is added to a nickel solution with an initial pH of 4·4–5·0, containing dimethylglyoxime and urea, dense crystalline nickel dimethylglyoximate precipitates quantitatively (see Table II). When the initial pH is greater than 5·0, precipitation

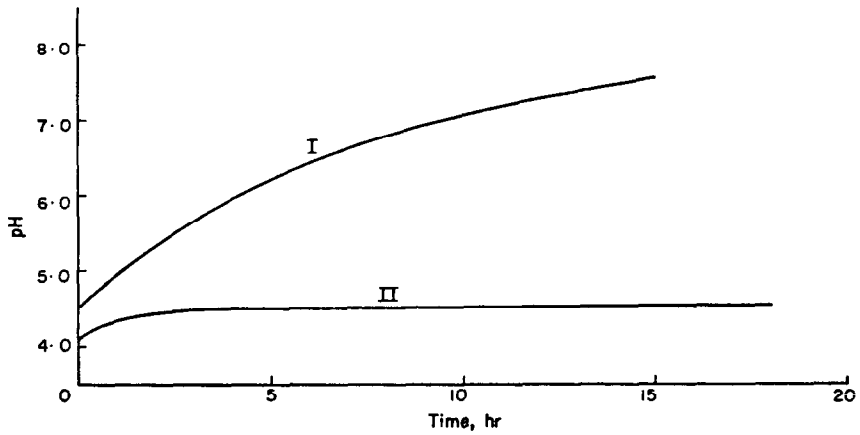

FIG. 1.—Effect of initial pH value on hydrolysis of urea by urease. I—initial pH 4·5; II—initial pH 4·1.

TABLE II.—EFFECT OF INITIAL pH VALUE

pH	Nickel		Difference, *mg*
	taken, *mg*	found, *mg*	
4·0	25·00	10·03	−14·97
4·1	25·00	23·90	−1·10
4·4	25·00	25·00	±0·00
4·7	25·00	25·05	+0·05
5·1*	25·00	24·97	−0·03
5·2*	25·00	25·03	+0·03
5·3†	25·00	—	—

* Ni-DMG precipitates rapidly.

† Precipitate grows before addition of urease and the precipitate is similar to that by the conventional method.

is rapid, and the product has an appearance similar to that of precipitates obtained by the usual methods.

Dependence on the concentration of urea and urease

As shown in Table III, satisfactory results are obtained when 10 g of urea are added to 250 ml of solution containing 20 ml of urease solution.

When 5 g of urea are added per 250 ml of the solution, the increase of pH of the solution is not sufficient for the quantitative precipitation of nickel dimethylglyoximate. When 40 g of urea are added not only are the results unsatisfactory, but the precipitate is flocculent, like those obtained by the usual procedures. It is not known whether this is due to the urea raising the pH by acting as a weak base, or to a decrease in the urease activity when the urea concentration is high; the results in Table II indicate that the former is the more likely explanation.

A certain amount of urease is necessary to give satisfactory decomposition of urea (Fig. 2 and Table IV). For 10 g of urea, at least 20 ml of 0·01 % urease solution should be added.

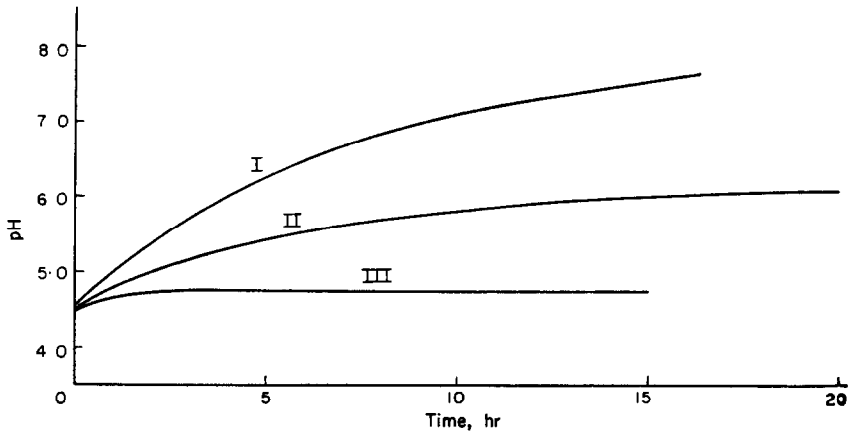

FIG. 2.—Effect of amount of urease on hydrolysis of 10 g of urea.
Urease solution: I—20 ml; II—10 ml; III—5 ml.

TABLE III.—EFFECT OF THE AMOUNT OF UREA

Urea added, *g*	Nickel		Difference, *mg*
	taken, *mg*	found, *mg*	
5	25·00	24·91	−0·09
10	25·00	24·99	−0·01
20	25·00	24·85	−0·15
40	25·00	22·72	−2·28

TABLE IV.—EFFECT OF THE UREASE CONCENTRATION

Urease added, *ml*	Nickel		Difference, *mg*
	taken, *mg*	found, *mg*	
5	25·00	16·39	−8·61
10	25·00	24·49	−0·51
20	25·00	24·99	−0·01

Effect of temperature

The optimum temperature for the hydrolysis of urea by urease is 35–40°. This was confirmed by following the change of pH at different temperatures, Fig. 3. When the precipitation is carried out from solution at 35–40°, the recovery of nickel ion as dimethylglyoximate is complete, as shown in Table V.

Effect of the concentration of dimethylglyoxime

From 13 to 20 ml of 1 % dimethylglyoxime solution is sufficient for the quantitative precipitation of 25 mg of nickel as nickel dimethylglyoximate (Table VI).

Determination of nickel

Table VII shows that satisfactory results are obtained for the precipitation of 5–25 mg of nickel by the procedure developed.

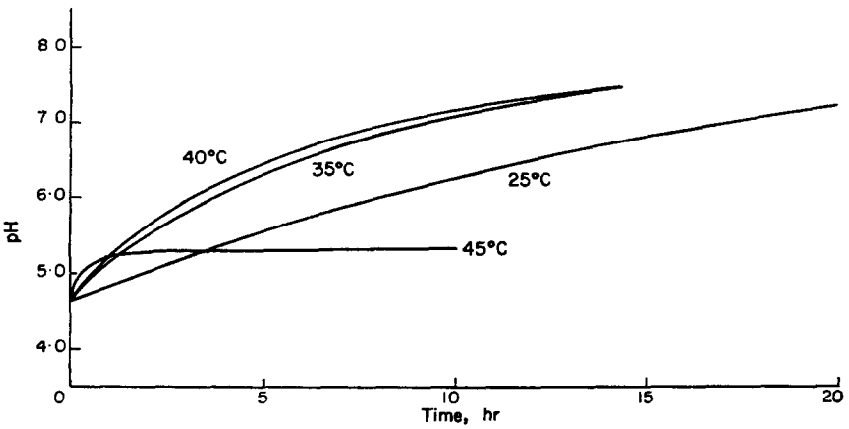

FIG. 3.—Effect of temperature on urease hydrolysis of urea.

TABLE V.—EFFECT OF TEMPERATURE

Temperature °C	Time, hr	Nickel		Difference, mg
		taken, mg	found, mg	
25	15	25·00	24·76	−0·24
25	26	25·00	25·58	+0·58
35	15	25·00	24·99	−0·01
40	15	25·00	25·03	+0·03
45	10	25·00	incomplete precipitation	

TABLE VI.—EFFECT OF DIMETHYLGLYOXIME CONCENTRATION

1%-DMG solution, ml	Nickel		Difference, mg
	taken, mg	found, mg	
10	25·00	24·31	−0·69
13	25·00	25·04	+0·04
15	25·00	24·99	−0·01
17	25·00	24·98	−0·02
20	25·00	25·03	+0·03

TABLE VII.—DETERMINATION OF NICKEL

Taken, mg	Found, mg	Difference, mg	In filtrate, mg
5·02	5·08	+0·06	0·065
10·04	10·00	−0·04	0·053
15·07	15·08	+0·01	0·023
20·09	20·14	+0·05	0·028
25·12	25·21	+0·09	0·022

Citric acid solution 5 ml; urea solution 50 ml; initial pH 4·4; dimethylglyoxime solution 15 ml; urease solution 20 ml; total volume *ca.* 250 ml; temperature 35°C for 15 hr.

TABLE VIII.—EFFECT OF OTHER IONS

Added			Nickel found, *mg**	Error, *mg*	Final pH
Ion	Amount, *mg*	Compound			
—	—	—	12·54	−0·02	8·4
As(III)	10	$NaAsO_2$	12·65	+0·09	8·6
As(V)	10	Na_2HAsO_4	12·62	+0·06	8·7
Cd(II)	10	$CdCl_2$	12·57	+0·01	8·6
Co(II)	10	$CoCl_2$	9·12	−3·44	5·7
	5		10·40	−2·16	6·4
	1		12·52	−0·04	8·3
Cu(II)	10	$CuCl_2$	12·98	+0·42	7·9
Fe(III)	10	$FeCl_3$	12·59	+0·03	8·7
Hg(II)	10	$HgCl_2$	2·98	−9·58	4·5
Pb(II)	5	$Pb(NO_3)_2$	12·52	−0·04	8·3
Pt(IV)	10	H_2PtCl_6	3·40	−9·16	4·5
Te(IV)	5	$TeCl_4$	11·18	−1·38	6·5
Cl^-	~650	NH_4Cl	12·51	−0·05	8·2
NO_3^-	~53	NH_4NO_3	12·50	−0·06	8·3
SO_4^{2-}	~470	$(NH_4)_2SO_4$	12·58	+0·02	7·3
$C_2H_3O_2^-$	~520	$NH_4C_2H_3O_2$	3·26	−9·30	5·1

* Nickel taken, 12·56 mg.

Effect of other ions

The effect of the presence of a number of other ions on the determination of 12·56 mg of nickel by the proposed procedure was examined. The results are summarized in Table VIII. Cobalt (5 mg), mercury (10 mg), platinum (10 mg) and tellurium (5 mg) inhibit the hydrolysis of urea and the precipitation of nickel dimethylglyoximate becomes incomplete. Arsenic, cadmium, iron, and lead do not affect the urease. Chloride, nitrate and sulphate do not interfere, but the pH of the solution does not increase in the presence of a large amount of acetate owing to its buffering action.

Acknowledgement—The authors wish to acknowledge the partial assistance of the Ministry of Education, Japan, in supporting the investigation described herein.

Zusammenfassung—Zur Harnstoffzersetzung bei der Fällung von Dimethylglyoximnickel aus homogener Lösung kann Urease verwendet werden. Die optimalen Versuchsbedingungen und eine Vorschrift, die gute Trennungen von anderen Ionen liefert, werden angegeben.

Résumé—On peut utiliser l'uréase pour décomposer l'urée dans la précipitation du diméthyglyoximate de nickel à partir d'une solution homogène. On décrit les conditions expérimentales optimales et une technique donnant de bonnes séparations à partir d'autres ions.

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ELEMENTAL ANALYSIS OF ORGANO-METALLIC COMPOUNDS

THE SIMULTANEOUS DETERMINATION OF CARBON, HYDROGEN AND OTHER ELEMENTS IN ONE WEIGHED SAMPLE

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Summary—A method is described for simultaneous gravimetric microdetermination of carbon, hydrogen and one or more hetero-elements in one weighed sample of organic substances. The method is based on pyrolytic combustion of the sample in a quartz container placed in an empty combustion tube. The carbon and hydrogen determination is completed as usual. Hetero-elements, in the form of volatile compounds, are retained in special previously weighed tubes inside the combustion tube. Hetero-elements forming non-volatile residues can be determined by the change in weight of the quartz sample-container. Volatile elements or compounds are determined by weighing the quartz insert tube. More than 40 elements in various combinations can be determined simultaneously with carbon and hydrogen.

THE number of elements which may be introduced into organic compounds has rapidly increased, and it is no exaggeration to say that almost all elements found in nature give a form of interaction (bonding) with organic compounds. This situation arises on the one hand from the extensive development of organo-metallic chemistry and on the other from the widespread use of organic reagents in inorganic chemistry, and has led to the need to determine quantitatively a wide variety of elements in organic compounds. In doing so it has given prominence to the methods of simultaneous determination of several elements in one weighed sample.

This paper deals with the most important type of simultaneous determination, the gravimetric determination of carbon, hydrogen, and some other elements in one weighed sample. The carbon and hydrogen determination itself is a classical example of the simultaneous determination of two elements, and early on, many attempts were made to determine a third element simultaneously as well.[1–4] In elemental microanalysis this has been achieved by M. O. Korshun and her coworkers[5–18] during the past two decades and later by others.[17,19–22] The purpose of this paper is to report on the general principles of this type of elemental analysis in its present state, to report the results achieved in our laboratory, and to describe briefly the main modes of operation.

So-called "pyrolytic combustion"[6,17,23,24] and gravimetric determination of the combustion products represents a general method of analysis accepted by us for simultaneous determination of carbon, hydrogen, and other elements (called hereafter "hetero-elements"). The reliability and universality of this combustion method in the determination of carbon and hydrogen have been confirmed by its application during many years. Its specific features, that no catalysts or oxidative packings are used in the combustion tube and that the substance is burned in a quartz container (Fig. 1)

past which flows a rapid stream of oxygen, offer great possibilities for simultaneous determinations. The main condition for simultaneous determinations, that the combustion is carried out in a container, seems to an uninformed analyst to be difficult, but in fact is an easy operation, which can be accomplished with simple manipulation for almost any organic compounds other than gaseous and highly explosive substances. It should be emphasized that pyrolytic combustion is the only method which provides

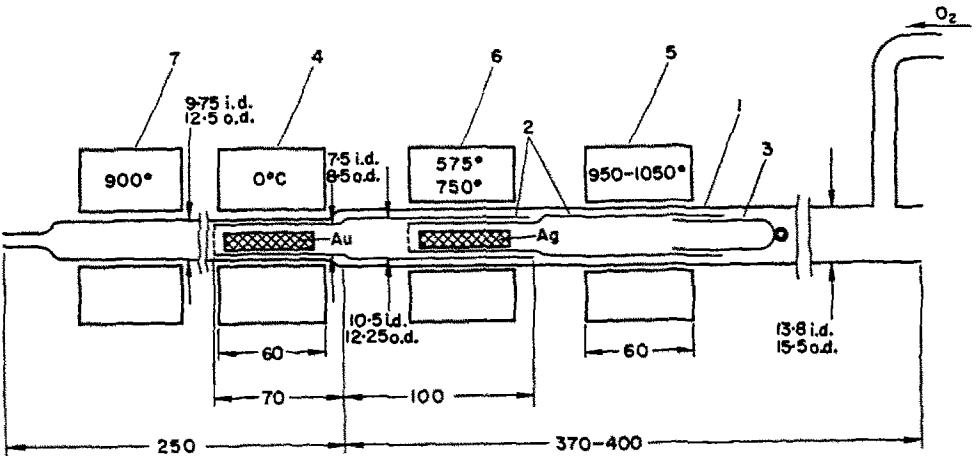

FIG. 1.—Apparatus for simultaneous determination of carbon, hydrogen and several hetero-elements in one weighed sample.

1. Combustion tube
2. Insert tubes
3. Container
4. Cooling device
5. Split-type furnace for combustion
6. Split-type furnace for heating silver
7. Split-type furnace for heating oxidizing zone

All dimensions are in mm.

simultaneous determination of several elements in a number of compounds that are difficult to analyse, such as substances that spray particles when they burn (ferrocene, carborane, *etc.*), volatile compounds (metal carbonyls, *etc.*) and materials inflammable in air. As a rule in simultaneous determination the combustion cannot be carried out as rapidly (3–5 min) as in simple carbon and hydrogen determinations.[25] Nevertheless, the possibility of determining from three to five elements by one combustion makes the slower procedure worthwhile.

Depending on the elemental composition of the substance, the combustion in oxygen can lead to formation of oxides, salts, solid solutions, molecular compounds, or elements in the free state, the products being both volatile and non-volatile compounds. The non-volatile, non-burning residue is most frequently an oxide, sometimes a sulphate, phosphate, borate or silicate, and more seldom an element in the free state. Volatile compounds liberated include halogens, mercury, and certain oxides (of sulphur, arsenic, rhenium, *etc.*).

The products of decomposition (oxidation) of organic compounds can be quantitatively separated and collected within the combustion tube* in several particular

* The absorption outside the combustion tube of volatile products containing hetero-elements has some disadvantages and is not used.

"zones to be weighed" (Fig. 1). These zones are a quartz container for combustion of samples, and quartz tubes, called insert tubes. The container is used for determining a non-burning non-volatile residue, and the insert tubes (over-lapping as shown in Fig. 1) contain suitable reagents (*e.g.*, metallic silver) for absorption of volatile combustion products, or are used to condense sublimates or to retain particles mechanically removed by the gas stream, and so on. Depending on its purpose the zone can be empty or filled, cooled or heated. As we have established earlier,[12] the presence of cooled zones in the combustion tubes does not interfere with the determination of carbon and hydrogen. The use of several "zones to be weighed" makes it possible to increase the number of hetero-elements to be determined simultaneously with carbon and hydrogen in one weighed sample, and in some cases (for antimony, manganese, *etc.*) to increase the accuracy of determination.

EXPERIMENTAL

Apparatus and reagents

The apparatus consists of an oxygen source, absorption tubes containing ascarite and anhydrone for preliminary drying and purification of oxygen, a combustion tube, quartz insert tubes and containers, Pregl absorption tubes for water, nitrogen oxides and carbon dioxide, filled with anhydrone, silica gel impregnated with saturated potassium dichromate solution in concentrated sulphuric acid, and ascarite and anhydrone respectively, and an aspirator. The quartz combustion tube has an enlarged section, into which the insert tube or tubes and the quartz sample-container are placed (Fig. 1).

The filling and temperature of the insert tube for various purposes are given in Table I. The insert tube and its filling will last for several determinations. For example, 30–50 halogen or sulphur determinations can be done with 1–1·5 g of silver gauze (0·1-mm wire) as absorbent. Separate tubes

TABLE I.—CONDITIONS FOR DETERMINATION OF HETERO-ELEMENTS FROM THE CHANGE IN WEIGHT OF THE INSERT TUBE

Elements to be determined	The insert tube	
	Temperature, °C	Filling
Chlorine, bromine, iodine	575°	silver gauze or foil
Chlorine, bromine, iodine	425°	silver-plated pumice
Sulphur	750°	silver gauze or foil
Rhenium	450°	silver gauze or foil
Arsenic, molybdenum, antimony or manganese traces	room temp.	none (or quartz wool)
Mercury	0° (cool in ice)	gold (or silver) gauze or foil

should be used for halogens and sulphur. If silvered pumice is used, one filling will do for 80–100 analyses, and the corrosion of the walls of the insert tube will be negligible, so the tube can be refilled and used again. An empty insert tube or one containing a filling that is not heated, *e.g.*, quartz wool or gold, will last for a long time (at least a year) and so will the filling. Containers of various lengths (60–90 mm) are used for the sample. They can be used repeatedly. A container can be used for as many as 12–15 residue determinations, being cleaned after each (cleaning with cotton wool, followed by ignition, or treatment with acid and washing with water usually suffices). Weight constancy of the container serves as a criterion for its continued use, but old containers can be used if a residue determination is not necessary. For heating the oxidation and absorption zones and for combustion of the sample, split-type furnaces, 60 mm long, are used.

The sample

Solids are weighed in the quartz sample-containers, which can be hung horizontally on the hooks of the balance pan. If the substance decomposes violently it is necessary to distribute it on a layer of crushed quartz; the sample can be spread over the quartz by tapping it after weighing it. In phosphorus determinations and analyses of substances which spray particles on combustion, it is advisable to cover the sample with another portion of the quartz and to weigh the container and contents again.

Samples of liquids are taken in a glass capillary, or better in a quartz capillary, which is usually weighed together with the container. The capillary with sample is placed, open end down, in the container. Sticky substances are introduced into the container by means of a thin quartz stick, which is weighed together with the container. If necessary, crushed quartz is added to liquid or sticky samples.

Combustion

At the beginning of the day's work a few mg (unweighed) of any standard substance should be burned to condition the apparatus. Then the first sample is burned off after the absorption tubes and insert tube have been weighed. The sample-container is placed 30 mm inside the insert tube and put together with it into the combustion tube. Oxygen is passed through the tube for 1–2 min and then the tube is connected to the Pregl tubes and the aspirator. The narrow part of the insert tube is heated (or cooled) to the proper temperature (see Table I), the movable furnace is set so that the open end of the container is 10–15 mm inside it, and is then moved over the container at a rate dictated by the behaviour of the sample. The burning of the substances is accompanied either by the appearance of red-hot carbon particles moving towards the container outlet, or by tongues of flame, or by carbonization of the substance without visible indications of burning. The combustion tempo can be controlled by moving the heater backwards and forwards. The open end of the container must be in the heated zone all the time and the combustion must proceed within the container. In the determination of hetero-elements which form readily condensed sublimates (As_2O_3, MoO_3, Re_2O_7) the combustion is carried out in an empty container, 60 mm long, which must be completely heated with the movable furnace, thus providing rapid and complete transport of the volatile oxide into the insert tube. For this purpose it is better to heat the container, after combustion, with two split-type funances, each 60 mm long. If after combustion a carbonaceous residue remains in the container, it is cooled for 1–2 min and then heated again until the carbon is all burned off. The combustion time usually varies from 15 to 30 min. If a rapid oxygen stream is used, it is not necessary to sweep out the products after combustion is complete. After combustion the absorption tubes are removed first, and the container and insert tube are allowed to cool in the combustion tube and then are taken out, "flamed" to remove any electrostatic charge, conditioned on a metal block, and weighed. A fresh portion of crushed quartz is used for each combustion. Insert tubes are given fresh filling or the old one is freed from sublimates as far as possible. Blank tests should not give weight changes of more than 10 and 20 μg for container and insert tube respectively. When certain elements (*e.g.*, antimony and manganese) are determined, the completeness of retention of the oxides in the container should be checked by weighing the empty insert tube. If the insert tube gains weight, this may be due to carry over of finely dispersed particles or by volatilization of the residue in the container at high temperatures. If the element is determined as a sublimate precipitated on the cold walls of the insert tube (*e.g.*, As_2O_3 or MoO_3), it is best to put a loose piece of quartz wool or other non-hygroscopic fibrous material in the insert tube outlet.

DISCUSSION AND RESULTS

The question of the weighing form for the various hetero-elements in some cases needs thorough study. In critical comparisons of the thermal, chemical and other properties of the proposed weighing forms with data obtained in gravimetric analysis, there are observed some discrepancies which can be explained by the variation in experimental conditions. Thus, almost all the gravimetric data[26] have been obtained by heating the substances in air. Under these conditions a reducing atmosphere can arise during ignition of the substances. The combustion in elemental analysis proceeds in an oxygen atmosphere, which may lead to predominant formation of the higher oxides if the element has a variable valency. At the temperatures of 950–1000° frequently used in the combustion of organo-metallic compounds, the possible formation of solid solutions, molecular compounds and silicates should also be taken into account, as the combustion takes place on the surface of quartz particles. For instance, in the determination of manganese, according to thermogravimetric data only Mn_3O_4 is expected to be formed above 950°, but X-ray analysis of the residue formed after combustion of organo-manganese compounds on quartz chips reveals the presence of either Mn_2O_3 or $Mn_7O_{10}.SiO_2$.[27] From the results of more than 50 analyses we are satisfied that the formula $Mn_7O_{10}.SiO_2$ gave the best agreement with the

analytical results for all three elements—carbon, hydrogen and manganese. The formation of compounds of silicate type is also observed with thallium, which gives a yellowish non-hygroscopic residue, whereas the oxide of thallium(I) must be gray or black. Sometimes the temperature used can be of decisive importance in a successful analysis. For example, to isolate palladium as metal it is necessary to carry out the combustion at 1050°, because at lower temperatures (900–950°) palladium is present partly as oxide.

The hygroscopicity of oxides under the conditions used for weighing them in elemental analysis should be studied in view of possible errors. Most of these errors are negligible, as they lie within the error limits permissible for the elemental analysis. In some cases, for instance in determination of aluminium or boron, errors due to the hygroscopicity of the oxides were studied in detail and eliminated during development of the analysis conditions.[15,18]

Over a period of about 10 years our laboratory has carried out thousands of simultaneous determinations of carbon, hydrogen and other elements. This type of analysis is a reliable well-developed method for the elements B, Al, Si, P, S, Cl, Ti, Cr, Mn, Fe, Ge, Br, Zr, Pd, Sn, Sb, I, W, Pt, Hg, Tl and Pb. Elements such as Be, Mg, As, Se, Co, Ni, Cu, Nb, Mo, Zn, Au, Ag, Cd, Hf, Ta and Bi are seldom met with, but there is no doubt as to the possibility of their determination by this method.

Analysis of substances containing halogen combined with either the organic part of the molecule or the hetero-element, gives another interesting possibility of simultaneous determination. In this case the combustion in the container has a remarkable advantage over that in a direct oxygen stream. Because of the high combustion temperature in the container (900–1000°), many halides, even volatile ones (iron(III), palladium, *etc.*) either decompose quantitatively within the heated container during combustion of the sample, or simply do not form, especially if the halogen is combined with the organic part of the molecule. Therefore, it is now possible to determine halogen and hetero-elements simultaneously with carbon and hydrogen for a large number of organo-metallic compounds. Simultaneous determination of carbon, hydrogen, halogen and another hetero-element in organic compounds of B, P, Ti, Si, Fe, Zr, Pt, Hg and Pd may be considered to be a standard method. There have been few simultaneous determinations applied to compounds of Pb, Ge, Cr, Cu, Co, Mo, W, *etc.*, and the field of application is therefore not yet well defined. Carbon, hydrogen, sulphur, and a hetero-element are determined in a similar manner, but there are somewhat fewer possibilities, as sulphates are usually more refractory than halides. There are, however, other specific possibilities of simultaneous determination. For example, in salts of organic sulphonic acids with alkali or alkaline earth metals, half of the sulphur is determined in the insert tube as silver sulphate and the other half in the container as metal sulphate. The amount of metal in the sample is calculated from the weight of the metal sulphate. With three "zones to be weighed", *i.e.*, the container and two insert tubes, it is possible to determine four or even five elements from one weighed sample. For example, in organo-mercury compounds it may be possible to determine carbon, hydrogen, halogen or sulphur, mercury, and one other element (B, P, Fe, *etc.*) as non-burning residue.

The weighing forms for hetero-elements are given in Table II. From Tables III and IV can be seen which element combinations are possible for simultaneous determinations, though these examples are far from exhausting the possibilities.

TABLE II.—HETERO-ELEMENTS AND THEIR WEIGHING FORMS

Element	Weighing form in the container	Weighing form in the insert tube
Pd, Ag, Pt, Au	Pd, Ag, Pt, Au	
Hg		Hg (gold amalgam)
Tl	Tl_2O SiO_2	
Be, Mg, Zn, Cd, Pb, Ni	BeO, MgO, ZnO, CdO, PbO, NiO	
B, Al, Cr, Fe, As, Rh, Eu, Er, Bi	B_2O_3, Al_2O_3, Cr_2O_3, Fe_2O_3, Rh_2O_3(?), Eu_2O_3, Er_2O_3, Bi_2O_3	As_2O_3
Mn	Mn_7O_{10}	Mn_7O_{10} (traces)
Si, Ti, Ge, Zr, Sn, Hf, Th, Se	SiO_2, TiO_2, GeO_2, ZrO_2, SnO_2, HfO_2, ThO_2	SeO_2
Sb	Sb_2O_4	Sb_2O_4 (traces)
P	P_2O_5	
Nb, Ta	Nb_2O_5, Ta_2O_5	
Mo, W	WO_3	MoO_3
S		SO_4 (Ag salt)
Cl, Br, I		Cl, Br, I (Ag salt)
Re		ReO_4 (Ag salt)
Co	Co_3O_4	

TABLE III.—THE SIMULTANEOUS DETERMINATION OF CARBON, HYDROGEN AND A HETERO-ELEMENT IN ONE WEIGHED SAMPLE

Compound and elements present, %	Carbon, %		Hydrogen, %		Hetero-element, %		Total %
	Found	Error	Found	Error	Found	Error	
$(i\text{-}C_3H_7O)_3Al$	52·73	−0·23	10·29	−0·07	13·14	−0·07	
C—52·96; H—10·36; Al—13·21	53·03	+0·07	10·53	+0·17	13·28	+0·07	
$C_5H_4COC_6H_5V(CO)_4$	57·91	+0·08	2·86	+0·15	15·78	+0·44	
C—57·83; H—2·71; V—15·34	57·72	−0·11	2·75	+0·04	15·72	+0·38	
$HOOCC_5H_4Mn(CO)_3$	43·51	−0·06	2·19	+0·16	22·37	+0·22	
C—43·57; H—2·03; Mn—22·15	43·68	+0·11	2·12	+0·09	22·31	+0·16	
4-OH-3—$CH_3CONHC_6H_3As(OH)_2$	34·74	−0·19	3·69	+0·03	27·23	0·00	
C—34·93; H—3·66; As—27·33	34·82	−0·11	3·81	+0·15	27·35	+0·12	
$Mo(CO)_6$	27·23	−0·07			36·15	−0·19	
C—27·30; Mo—36·34	27·28	−0·02			36·22	−0·12	
π-D*—Rh—C_5H_5-π	48·94	−0·25	5·34	+0·11	27·77	−0·33	
C—49·19; H—5·23; Rh—28·10	48·87	−0·32	5·24	+0·01	27·98	−0·12	
3,5-$(CH_3)_2$—4—NO—$C_6H_2OSn(C_6H_5)_3$	62·31	−0·12	4·64	+0·01	23·81	+0·06	
C—62·43; H—4·63; Sn—23·75	62·41	−0·02	4·54	−0·09	23·78	+0·03	
$(C_6H_5)_3Sb$	61·21	−0·02	4·36	+0·08	34·43	−0·06	100·00
C—61·23; H—4·28; Sb—34·49	61·35	+0·12	4·35	+0·07	34·15	−0·34	99·85
$C_5H_5W(CO)_3C_6H_5$	40·75	−0·25	2·36	−0·10	44·68	−0·16	
C—41·00; H—2·46; W—44·84	40·76	−0·24	2·40	−0·06	44·56	−0·28	
$C_5H_5Re(CO)_3$	28·61	−0·03	1·48	−0·02	55·36	−0·18	
C—28·64; H—1·50; Re—55·54	28·83	+0·19	1·55	+0·05	55·17	−0·37	
C_5H_5Tl	22·42	+0·14	1·94	+0·07	75·85	0·00	100·21
C—22·28; H—1·87; Tl—75·85	22·36	+0·08	1·92	+0·05	75·87	+0·02	100·15
$4\text{-}ONC_6H_4PbO(C_6H_5)_3$	51·39	−0·04	3·51	+0·12	36·59	−0·38	
C—51·43; H—3·39; Pb—36·97	51·49	+0·06	3·48	+0·09	36·83	−0·14	
$(C_6H_5)_3Bi$	48·81	−0·29	3·43	0·00	47·41	−0·06	99·65
C—49·10; H—3·43; Bi—47·47	49·11	+0·01	3·40	−0·03	47·62	+0·15	100·13

* Durouquinone

TABLE IV.—THE SIMULTANEOUS DETERMINATION OF CARBON, HYDROGEN AND SEVERAL HETERO-ELEMENTS IN ONE WEIGHED SAMPLE

Compound and Elements present, %	Carbon, %		Hydrogen, %		Hetero-elements, %						Total, %
					Non-volatile residue		Mercury		Halogen or sulphur		
	Found	Error	Found	Error	Found	Error	Found	Error	Found	Error	
o-$CH_3CB_{10}H_{10}CHgBr$	8·12	−0·11	2·94	−0·05	24·92	+0·22	45·64	−0·18	17·97	−0·28	99·59
C—8·23; H—2·99; B—24·71; Br—18·25; Hg—45·82	8·16	−0·07	3·06	+0·07	24·98	+0·27	45·59	−0·23	17·90	−0·35	99·69
m-$HCB_{10}H_9ClCH$	13·50	+0·06	6·25	+0·05	61·01	+0·48	—	—	19·91	+0·08	100·67
C—13·44; H—6·20; B—60·53; Cl—19·83	13·32	−0·12	6·44	+0·24	61·02	+0·49	—	—	19·71	−0·12	100·49
$(C_6H_5)_3SiCH{=}CHHgCl$	25·58	+0·11	4·67	+0·13	7·05	−0·39	52·72	−0·44	9·42	+0·03	99·44
C—25·47; H—4·54; Cl—9·39; Si—7·44; Hg—53·16	25·43	−0·04	4·83	+0·29	7·18	−0·26	52·47	−0·69	8·99	−0·40	98·90
$(CH_2CH{=}CH)_2P{\cdot}CHI$	40·36	−0·17	6·23	+0·11	10·51	+0·05	—	—	42·63	−0·19	99·73
C—40·53; H—6·12; P—10·46; I—42·82	40·50	−0·03	6·24	+0·12	10·62	+0·16	—	—	42·69	−0·13	100·05
$(P{-}CH_2C_6H_4SO_3)_2Ba$	34·92	−0·12	2·95	+0·04	28·44	−0·20	—	—	13·19*	−0·16	—
C—35·04; H—2·91; Ba—28·64; S—13·35	35·09	+0·05	2·96	+0·05	28·88	+0·24	—	—	13·10*	−0·25	—
†$(C_4H_9O)_2Ti{-}O{-}Ti(C_4H_9O)_2{-}O{-}Ti{-}(C_4H_9O)_2$ (Cl, Cl)	41·98	−0·06	7·91	−0·03	20·70	−0·28	—	—	10·26	−0·09	—
C—42·04; H—7·94; Cl—10·35; Ti—20·98	41·86	−0·18	7·93	−0·01	20·81	−0·17	—	—	10·35	0·00	—
$(C_6H_5)_3CrI$	43·00	0·00	3·65	+0·04	15·07	−0·48	—	—	37·67	−0·24	99·35
C—43·00; H—3·61; Cr—15·55; I—37·87											
$ClC_5H_4FeC_5H_4HgCl$	26·51	+0·15	1·79	+0·02	12·35	+0·09	43·52	−0·52	15·70	+0·13	99·87
C—26·36; H—1·77; Cl—15·57; Hg—44·04; Fe—12·26	26·50	+0·14	1·80	+0·03	12·52	+0·26	43·75	−0·29	15·80	+0·23	100·37
$(p{-}ClC_6H_4)_2GeO$	46·43	+0·20	2·73	+0·15	23·00	−0·29	—	—	22·75	0·00	—
C—46·23; H—2·58; Cl—22·75; Ge—23·29	46·45	+0·22	2·80	+0·22	23·10	−0·19	—	—	22·78	+0·03	—
$(C_5H_5)_2ZrBr_2$	31·66	+0·17	2·56*	−0·08	24·10	+0·16	—	—	41·86	−0·07	100·18
C—31·49; H—2·64; Zr—23·94; Br—41·93	31·66	+0·17	2·67	+0·03	24·07	+0·13	—	—	41·83	−0·10	100·23
$(\pi\text{-}C_3H_5PdCl)_2$	19·66	0·00	2·65	−0·10	58·48	+0·25	—	—	19·25	−0·10	100·04
C—19·66; H—2·75; Pd—58·23; Cl—19·35	19·64	−0·02	2·70	−0·05	58·38	+0·15	—	—	19·29	−0·06	100·01
$(C_5H_5)_2HfCl_2$	31·73	+0·10	2·77	+0·11	47·02	−0·02	—	—	19·13	+0·45	100·55
C—31·63; H—2·66; Hf—47·04; Cl—18·68	31·61	−0·02	2·61	−0·05	46·70	−0·34	—	—	18·76	+0·08	99·58
$(CH_3)_3PtBr$	11·49	−0·03	3·01	+0·20	60·77	−0·18	—	—	24·92	−0·08	100·19
C—11·52; H—2·81; Br—25·00; Pt—60·95	11·30	−0·22	2·87	+0·06	60·68	−0·27	—	—	24·76	−0·24	99·61

* Calculated from the weight of Ag_2SO_4 and of the $BaSO_4$ residue.

† Cl position is not established.

ERRORS IN SIMULTANEOUS DETERMINATIONS

In the gravimetric determination of those elements that have a weighing form with a favourable conversion factor, the absolute error does not exceed the ±0·3% accepted in microanalysis. If the factor is near to unity (determination of rhenium, tungsten, bismuth and other heavy elements) or equal to it (determination of elements in the free state, *e.g.*, mercury and palladium), the permissible errors may be as great as 0·7–1%, but such large deviations are seldom found in practice.

To obtain correct results for carbon and hydrogen, empirical corrections are made to the weights of carbon dioxide and water. They may be calculated from the results obtained for combustion of standard substances under similar conditions. These corrections are necessary because of (*a*) the large volume of oxygen (500–1000 ml) used, (*b*) the use of open Pregl tubes, and (*c*) temperature differences between laboratory and balance room. The corrections are well reproducible and do not usually exceed 70 μg for carbon dioxide and 150 μg for water. Corrections for hetero-elements are not made, except for silicon compounds, where they are necessitated by the particular properties of the residue.

It is evident that the simultaneous determinations of element gives wide and accurate information about the elemental composition of a substance without much expenditure of work and time by the analyst, and, which is particularly valuable, requires only a few mg of substance. Simultaneous determinations are especially useful in analysis of compounds containing several hetero-elements, which occur more and more frequently in organo-metallic chemistry.

Zusammenfassung—Eine Methode zur gleichzeitigen gravimetrischen Mikrobestimmung von Kohlenstoff, Wasserstoff und einem oder mehreren Heteroelementen in einer Einwaage von organischen Substanzen wird beschrieben. Die Methode beruht auf pyrolytischem Aufschluß der Probe in einem Quarzbehälter, der in einem leeren Verbrennungsrohr untergebracht wird. Heteroelemente werden als flüchtige oder nichtflüchtige Verbindungen in besonderen, vorher gewogenen Röhrchen im Verbrennungsrohr gesammelt. Die Kohlenstoff- und Wasserstoffbestimmung wird wie üblich erledigt. Nichtflüchtige Rückstände bildende Heteroelemente können durch die Gewichtsänderung des Quarz-Cehälter bestimmt werden. Mehr als 40 Elemente können in verschiedenen Kombinationen zusammen mit Kohlenstoff und Wasserstoff bestimmt werden.

Résumé—On décrit une méthode de microdétermination gravimétrique simultanée du carbone, de l'hydrogène et d'un ou plusieurs hétéro-éléments dans une pesée d'échantillon de substance organique. La méthode est basée sur la combustion pyrolytique de l'échantillon dans un récipient en quartz placé dans un tube à combustion vide. Les hétéro-éléments, sous forme de composés volatils ou non, sont retenus à l'intérieur du tube à combustion par des tubes spéciaux préalablement pesés. Le dosage du carbone et de l'hydrogène est achevé comme d'habitude. On peut doser les hétéro-éléments formant des résidus non volatils par la variation de poids du récipient en quartz contenant l'échantillon. On peut doser plus de 40 éléments dans des combinaisons diverses simultanément avec le carbone et l'hydrogène.

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APPLICATION OF THERMOELECTRIC POTENTIAL MEASUREMENTS IN CHEMICAL ANALYSIS—II*

DETERMINATION OF ALUMINIUM IN IRON ALLOYS

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Summary—A method is proposed for the rapid determination of aluminium in iron alloys by means of thermoelectric potential measurement. An instrument has been modified, and a method devised for thermoelectro-analytical measurements. The thermoelectric potential of iron–germanium and iron–zinc alloys has been measured, and an attempt made at a theoretical explanation of the influence of alloying elements on the thermoelectric properties of transition metals.

THERMOELECTRIC POTENTIAL (TEP) measurements may be used in analysis for sorting materials differing in chemical composition, without determining any one of the components,[1–9] for determining alterations in the metallographic composition,[10–15] or determining one of the components of the sample.

The quantitative determination of a sample component by TEP measurement has up to now been limited to the determination of silicon or carbon in iron alloys.[16–20]

Since, after several years of practical use, the thermoelectric method has been found to be very advantageous because of its speed, precision and reliability, it has been further studied to find other applications and to establish the theoretical fundamentals for the elucidation of the influence of alloying elements on the thermoelectric properties of the alloy.

EXPERIMENTAL

Apparatus

The assembly used has been described earlier.[16] Only the arrangement of the hot electrode (Fig. 1), the manner of measuring its temperature and the measuring assembly proper have been modified. The hot electrode is located in a metal mantle which is movable vertically on a support (Fig. 2). The tempered cold electrode is located in the base of this support. The temperature of the silver point of the hot electrode is measured by a silver–constantan thermocouple with its hot junction pressed into the silver electrode point. The sensitivity of temperature measurement has been enhanced by using a galvanometer with compensation wiring (Fig. 3).

The resistance R_2 is placed in series with the temperature-measuring galvanometer: a d.c. voltage, opposed to the TEP of the silver–constantan thermocouple, is applied to this resistance (position 1—*measurement*—on switch K_2). The galvanometer G_2 then measures the difference of the two voltages. In this way the full sensitivity of the galvanometer can be utilized. To check the compensation voltage during measurement the two-pole switch K_2K_3 is used. In the instrument designed, *e.g.*, for industrial routine checking of the silicon or aluminium content of steel, compensation wiring is also used in the TEP-measuring circuit. The compensation voltage is then selected so that zero on the galvanometer corresponds to the minimum content of the element being determined, and the temperature difference

* Part I—*Talanta*, 1964, **11**, 1127.

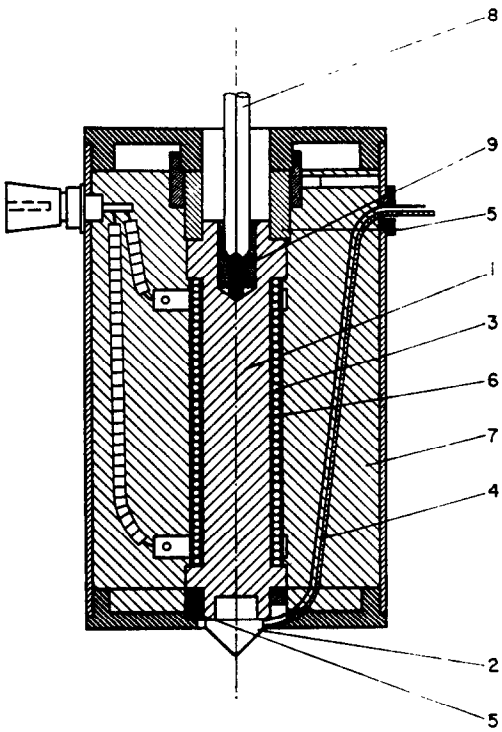

FIG. 1.—"Hot" electrode.
1—Copper rod; *2*—silver contact; *3*—heating spiral; *4*—silver–constantan thermocouple; *5*—ceramic isolation rings; *6*—glass fabric; *7*—glass wool; *8*—contact thermometer; *9*—low-melting alloy bath.

between the electrodes is chosen, for a given galvanometer sensitivity, so the the maximum content of the element determined gives full-scale deflection on the galvanometer. In this way the sensitivity of the determination can be increased.

Alloys

Iron–aluminium alloy. Samples (300 g) were melted down in a vacuum arc furnace (Heraeus L 200 H) in an argon atmosphere, with a tungsten electrode. To achieve good homogeneity of the casting, the sample was turned and remelted several times.

Iron–germanium alloy. Samples were prepared in the same way as iron–aluminium samples, but the argon used was repurified by passage over red-hot calcium.

Zinc–iron alloy. Samples were melted down in an electric induction furnace (type ACES) in a normal atmosphere and cast immediately from the furnace at 1550° into a metal mould.

The raw materials used for the alloys mentioned were Arema-type iron (Czechoslovak Standard ČSN 12013: Mn 0·27–0·33%, C 0·02–0·07%, P max. 0·03%, Si max. 0·01%, Cr, Ni max. 0·01%), aluminium of technical purity, electrolytic zinc and germanium (99·9% purity). After grinding with a disc-type grinding machine, the side of the samples which was to come into contact with the hot electrode was fine-ground with abrasive paper.

Procedure

Set on the contact thermometer a temperature about 2° higher (for iron alloys) than the temperature at which it is wished to read the TEP value of the sample to be tested. Temper the sample to 20° on the electrode E_1 and then apply electrode E_2. The TEP value on galvanometer G_1 must always be read at the same deflection of galvanometer G_2 used to measure the temperature. When compensation wiring is used in the circuit of the temperature-measuring thermocouple, there is no need to correct for the error caused by an incorrect temperature difference between the electrodes. If a thermostat

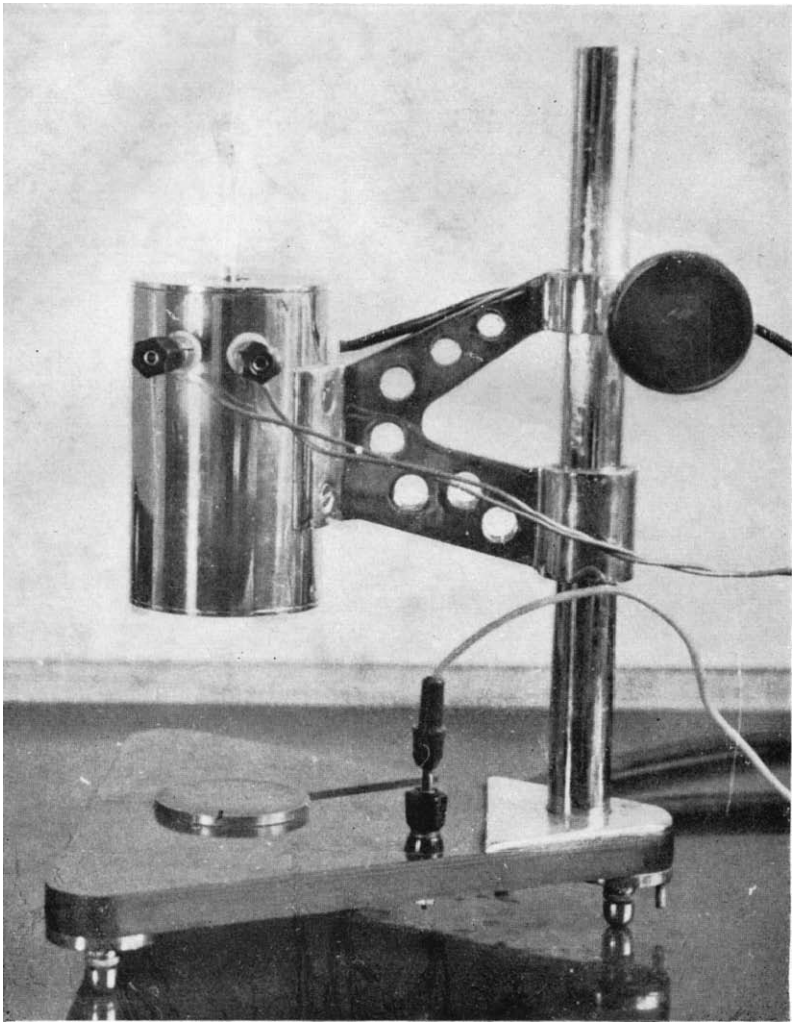

FIG. 2.—Support with the hot and cold electrodes.

is used and measurement on small samples is not repeated too quickly, the cold electrode will be sufficiently tempered and its temperature will not vary during the measurement. The TEP values mentioned in the following are always the mean of three values. According to convention, the TEP is taken as positive if the cooler electrode (E_1) is positive.

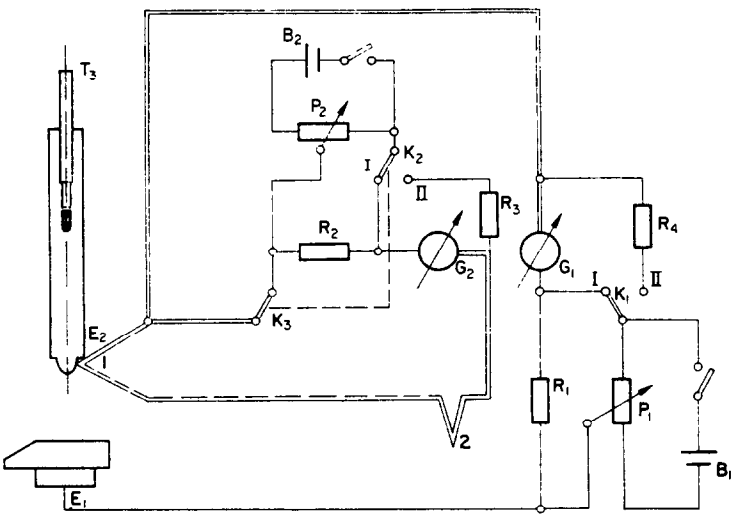

FIG. 3.—Diagram of the measuring circuit of the thermoelectric instrument designed for routine testing.
1,2—Hot and cold junctions of the Ag–constantan thermocouple; E_2,E_1—hot and cold electrodes; B_1,B_2—dry cell 1·5 V; G_1—Multiflex galvanometer, internal resistance 1300 Ω, sensitivity 4×10^{-9} A/mm; G_2—Titroskop-type galvanometer, internal resistance 320 Ω, sensitivity 9×10^{-9} A/mm; P_1,P_2—10 kΩ potentiometers; K_2,K_3—two-pole switch; K_1—one-pole switch; resistances: R_1—50 Ω; R_2—150 Ω; R_3,R_4—variable resistances 10 kΩ; ═══ Ag wire; ┈┈┈ constantan wire.

RESULTS AND DISCUSSION

We have mainly studied aluminium and its influence on the TEP of iron. It was found that aluminium shifts the TEP value of iron towards negative values more than silicon does (Fig. 4). Thus aluminium would interfere in the thermoelectric determination of silicon (positive error) in iron alloys. On the other hand, the exceptional influence of aluminium may be utilized for its sensitive thermoelectric determination in iron in the absence of silicon or with a constant amount of it present. The optimum range of Δt values for this determination is 200–260°. The calibration curve for the determination of aluminium, constructed for $\Delta t = 200°$ is shown in Fig. 7.

The thermoelectric method of aluminium determination has been applied to samples of different chemical composition and prepared in different ways. The results are given in Table I. As expected, larger chromium contents (samples 2K, 3K) interfere in the determination of aluminium (as they do in the determination of silicon in iron alloys) causing a negative error. For the other alloys the precision of the determination is satisfactory and the results are reproducible.

Among the other elements forming solid solutions with iron, germanium (Fig. 5) and zinc (Fig. 6) were studied. These metals also decrease the TEP value of iron. However, the influence of germanium is far smaller than that of silicon (Fig. 7). The influence of zinc on the TEP value is slight even with high concentrations (3·5%) (Fig. 7).

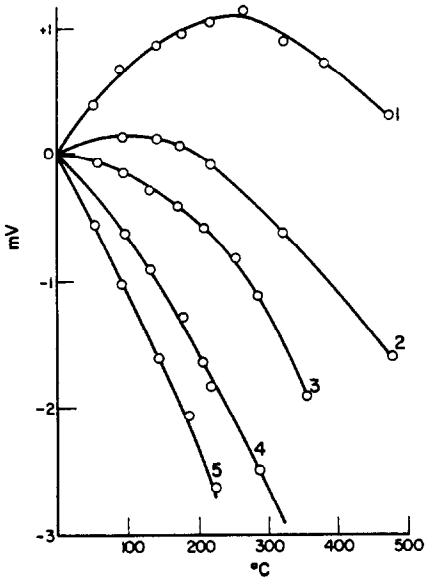

FIG. 4.—Dependence of the thermoelectric potential of iron with varying aluminium content, on the temperature difference between the hot and cold contact (Δt).

ANALYSIS OF THE ALLOYS

	Al,%	Mn,%	C,%	Si,%
1	0	0·32	0·06	0·01
2	0·48	0·32	0·06	0·01
3	0·72	0·27	0·05	0·008
4	1·74	0·27	0·05	0·009
5	2·95	0·28	0·07	0·01

All the samples contained P max. 0·03% and S max. 0·03%, other elements, *e.g.*, Ni, Cr, less than 0·01%

TABLE I

Sample No.	Chemical composition, %							Al found		Error, %	Relative error, %
	Mn	C	P	S	Si	Cr	Ni	Chemical	TEP		
1V	0·33	0·04	0·018	0·03	0·01 max.	0·01 max.	—	0·16	0·16	0	0
2V	0·30	0·05	0·020	0·04	0·01 max.	0·01 max.	—	0·62	0·62	0	0
3V	0·30	0·03	0·015	0·04	0·01 max.	0·01 max.	—	1·20	1·22	+0·02	+1·6
4V	0·30	0·05	0·022	0·03	0·01 max.	0·01 max.	—	2·40	2·45	+0·05	+2·1
1K	0·73	0·52	—	—	0·04	0·08	0·08	0·20	0·21	+0·01	+4·7
2K	0·44	0·32	—	—	0·21	1·87	0·36	0·90	0·69	−0·21	−23·1
3K	0·74	0·30	—	—	0·20	1·63	0·49	1·22	0·88	−0·34	−27·9

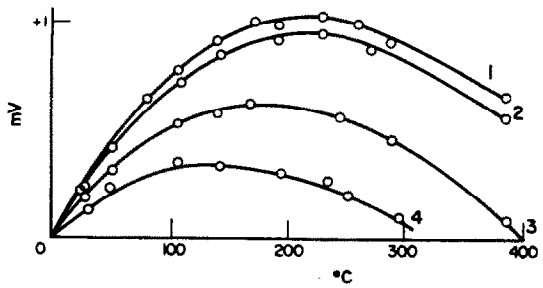

FIG. 5.—Dependence of the TEP value of Fe–Ge alloys on the temperature difference between the contacts of the electrode and sample.

ANALYSIS OF THE ALLOYS

	Ge,%	Mn,%	C,%	Si,%
1	0·01	0·28	0·02	0·01
2	0·02	0·30	0·02	0·01
3	0·60	0·28	0·05	0·01
4	0·95	0·30	0·05	0·01

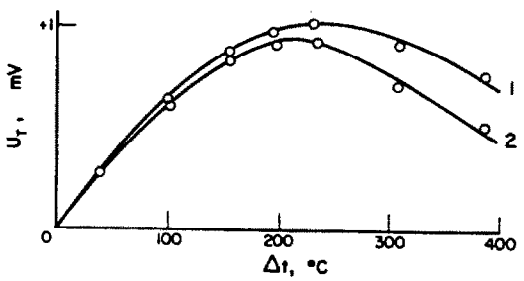

FIG. 6.—Dependence of the TEP value of Fe–Zn alloys on Δt.

ANALYSIS OF THE ALLOYS

	Zn,%	Mn,%	C,%	Si,%
1	0·60	0·30	0·05	0·01
2	3·5	0·28	0·06	0·01

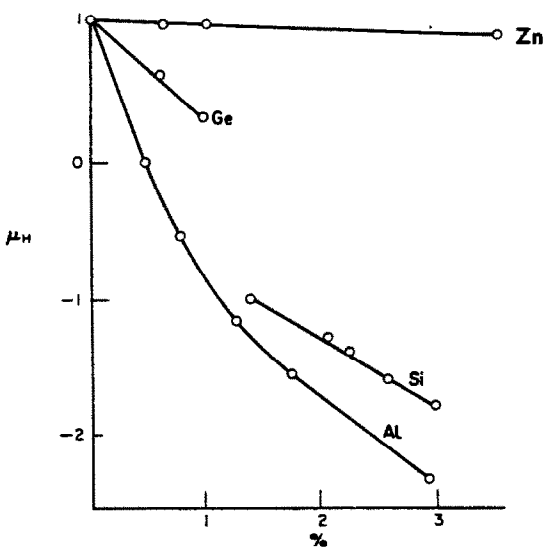

FIG. 7.—Dependence of the TEP value of iron on the content of Zn, Ge, Si and Al at $\Delta t = 200°C$.

The influence of carbon, manganese, phosphorus and sulphur on the TEP of iron has already been discussed.[16] The TEP value of iron alloys, moreover, is influenced to a small degree[31] by molybdenum (up to 5% w/w), vanadium (up to 18% w/w), nickel (up to 2·5% w/w) and tungsten (up to 5% w/w). These elements, therefore, will not interfere in the thermoelectric determination of aluminium or silicon in iron. On the other hand, chromium shifts the TEP value of iron distinctly toward positive values. Thus chromium in the range 0–1% interferes, but more than 1% of chromium does not have such a marked influence.[31] The influence of chromium may be eliminated by constructing a calibration curve by means of standards with about the same chromium content as that expected in the samples.

Existing data on the influence of germanium on the TEP value of iron[32,33] concerned alloys with compositions outside the solid solution range. The TEP values of iron–germanium alloys with germanium contents up to 1% were measured. The influence of germanium on the TEP value of iron is less than that of silicon.

It has already been stated[16] that the extraordinary influence of silicon on the TEP value of iron alloys cannot be explained by the high thermoelectric potential of silicon alone. That such a hypothesis[20,34–36] is incorrect has also been confirmed by TEP measurements on iron–aluminium and iron–germanium alloys. The explanation of the influence of alloying elements on the thermoelectric properties of the alloy, within the limits of solid-state solubility, must take into account the electron structure of the alloying elements and of the base metal. The theory of thermoelectric phenomena for metals is somewhat different from that used for semiconductors, *e.g.*, by Tauc.[21] The fundamental factors have been presented by Wilson,[22] Mott and Jones,[23] MacDonald[24] and others.[25–30]

Mott and Jones[23] show that the thermoelectric potential for a transition metal alloy is dependent on the extent to which the conducting *d*-band is filled with electrons. Iron has a partially filled *d*-band; if it is mixed with an element capable of filling the band, large negative values of the thermoelectric potential result. If the alloying element has a prevailing positive hole configuration the thermoelectric potential is either unaffected or becomes positive. Aluminium is effective in filling the band, and the thermoelectric potential for iron-aluminium alloys is strongly dependent on the composition. Zinc (Fig. 7), nickel, tungsten, vanadium and molybdenum have little effect, but chromium brings about a shift to more positive values. Silicon and germanium give rise to a negative shift, presumably because some of their *s* electrons contribute to the filling of the iron *d*-band.

The thermoelectric effect is also dependent on other factors besides chemical composition, *e.g.*, the structure of the sample, deformations and lattice defects, rate of cooling, and subsequent mechanical treatment. The method is therefore most suitable if molten samples can be taken and treated identically by the analyst. Of other electron transport effects, the Hall effect may be applied to chemical analysis.[37,38]

Zusammenfassung—Eine Methode zur raschen Bestimmung von Aluminium in Eisenlegierungen durch Thermokraftmessungen wird beschrieben. Ein Meßinstrument wurde umgestaltet und ein Verfahren für thermoelektrisch-analytische Messungen entwickelt. Die Thermokraft von Eisen-Germanium- und Eisen-Zink-Legierungen wurde gemessen und versucht, den Einfluß zulegierter Elemente auf die thermoelektrischen Eigenschaften von Übergangsmetallen theoretisch zu erklären.

Résumé—On propose une méthode pour le dosage rapide de l'aluminium dans les alliages de fer au moyen de mesures de potentiel thermoélectrique. On a modifié un instrument et élaboré une méthode pour les mesures thermo-électro-analytiques. On a mesuré le potentiel thermoélectrique d'alliages fer-germanium et fer-zinc et tenté une explication théorique de l'influence des éléments alliés sur les propriétés thermoélectriques des métaux de transition.

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MICRODETERMINATION OF THE AZIDE GROUP IN ORGANIC COMPOUNDS

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Summary—A simple, rapid and accurate micro-method for the analysis of mono- and diazide organic compounds is described. It is based on the Curtius rearrangement reaction. Glacial acetic acid is found to be the best decomposition medium. The acyl azide function yields two nitrogen atoms per azide group, but the diazides investigated ultimately give five nitrogen atoms per group on oxidation of their decomposition products, with acidified cerium(IV) sulphate solution. The decomposition time varies from 10 min for monoazides to 20 min for diazides. Accurate results were obtained for a representative series of 18 mono- and diazides.

RELATIVELY few methods have been reported for the determination of the azide group in organic compounds, and none is available on the micro scale. A method based on the reduction of azides by arsenite,[1] and another involving decomposition followed by Kjeldahl nitrogen determination on the residue,[2] have been reported. The latter method, though successful, is time-consuming and tedious. None of these methods has so far been applied on the micro scale.

The recently growing interest, in this department, in the synthesis of organic azides, necessitated the development of an accurate and rapid method for the determination of the azide group in such unstable compounds. The Curtius rearrangement reaction,[3] known to be specific for the azide group, appeared to suit our purpose, and had occasionally been used for the analysis of azide compounds on the macro scale.[4,5] Therefore the present work was undertaken to develop a micro method for the analysis of organic azides. The effect of the decomposition medium, the decomposition time, and some possible interferences were studied in order to establish the optimum procedural conditions.

EXPERIMENTAL

Reagents

Glacial acetic acid, 50% potassium hydroxide, 1*M* cerium(IV) sulphate in 20% sulphuric acid, solid carbon dioxide; all reagents were of analytical grade unless otherwise specified.

Apparatus

A diagram of the apparatus used is shown in Fig. 1. It consists of decomposition (A) and oxidation (B) vessels (10 × 2 cm), a trap (C), a small glass funnel (D), a Dewar flask (containing solid carbon dioxide), a micro burner and a micro nitrometer (1·50-ml capacity with 0·01-ml divisions). All the connections are Quickfit except those to the Dewar flask and the nitrometer, which were made of polythene tubing.

Procedure

Assemble the clean apparatus as shown in Fig. 1. Introduce not more than 5 mg of the sample into the decomposition vessel. Displace the air in the system with carbon dioxide. Introduce 2 ml of glacial acetic acid into the decomposition vessel through the funnel. Gently heat the reaction

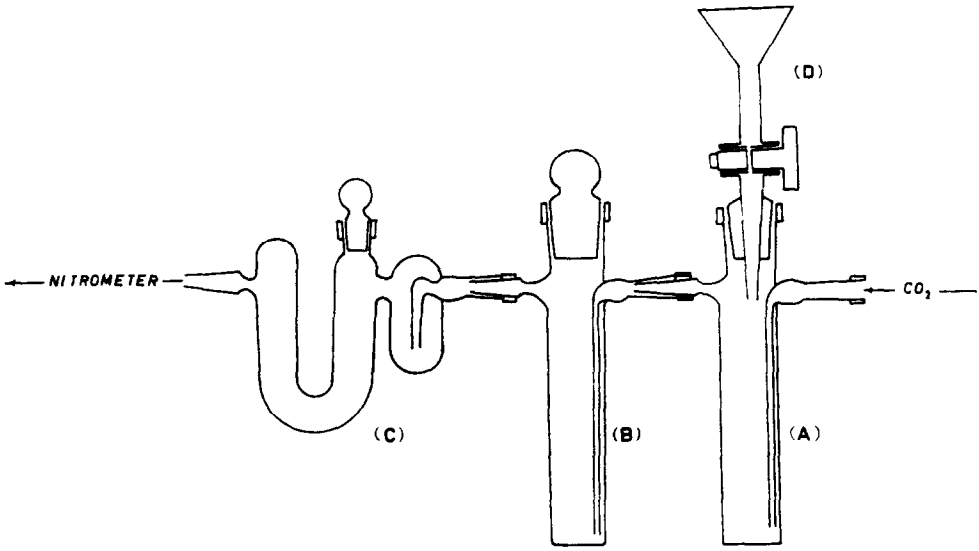


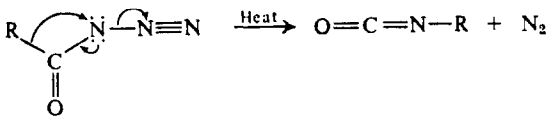
FIG. 1.—Apparatus for azide determination.
(A) Decomposition vessel; (B) oxidation vessel; (C) trap; (D) funnel.

mixture, for 10 min in the case of monoazides and 20 min for diazides, using a micro burner. Add one drop of cerium(IV) sulphate solution to the reaction mixture. Sweep the decomposition gases (for 5 min at a rate of 100 bubbles/min) through the oxidation vessel containing 5 ml of cerium(IV) sulphate solution. Collect the nitrogen gas produced, over concentrated potassium hydroxide solution in a micro nitrometer. Carry out a blank experiment under identical conditions.

RESULTS AND DISCUSSION

Decomposition medium

The Curtius rearrangement reaction[3,6] is essentially the decomposition of azide in acid medium to yield an isocyanate and nitrogen by thermolysis as follows:



The isocyanate is either isolated as such in inert solvents, *e.g.*, benzene and chloroform, or as derivatives, depending on the medium (*e.g.*, in alcohol, urethane or urea is obtained). This rearrangement is highly hazardous in the absence of solvents. In sulphuric acid medium the rearrangement sometimes takes place with partial decarbonylation to give a mixture of carbon monoxide and nitrogen.[7]

A decomposition medium in which the azide decomposes to liberate only two-thirds of its nitrogen content is a desideratum. The decomposition of some test compounds by heating in different media (basic, neutral and acidic) has thus been studied to determine the most suitable medium.

Decomposition in a basic medium. A 20% aqueous sodium hydroxide solution was tried, but no nitrogen was evolved. This may be attributed to the formation of sodium azide according to the reaction

$$RCON_3 + 2NaOH \rightarrow RCOONa + H_2O + NaN_3.$$

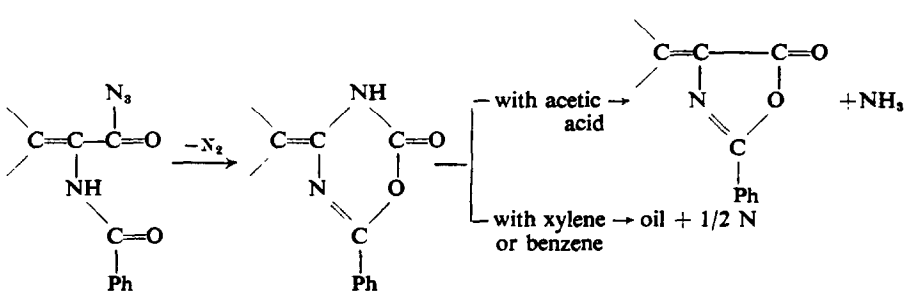
It was then thought to exploit this displacement reaction to produce sodium azide and then oxidize it to elementary nitrogen with cerium(IV) sulphate. The volume of nitrogen liberated was, however, more than the value calculated for two nitrogen atoms per azide group and less than that for three atoms per group. These invariably low values for nitrogen are attributed to incomplete hydrolysis rather than to the incomplete oxidation of sodium azide with cerium(IV) sulphate, which is shown to proceed quantitatively on the micro scale (*vide infra*). On the addition of the oxidizing agent, the unhydrolysed azide undergoes normal decomposition (loss of 2 nitrogen atoms/azide group) along with the oxidation of the sodium azide produced (loss of 3 nitrogen atoms/azide group). This assumption is in agreement with the finding of Forster and Van Gelderen[8] that the attack on α-azido carbonyl compounds by hydroxyl ions results in small amounts of displacement.

Organic bases such as aliphatic and aromatic amines were next tried as decomposition media. With aliphatic amines (*e.g.*, n-propylamine) no nitrogen was evolved. It seems that the basicity of such an aliphatic amine leads to the following reaction competing successfully with the azide decomposition.[9]

$$RCON_3 + R'NH_2 \rightarrow RCONHR' + HN_3$$
$$R'NH_2 + HN_3 \rightarrow [R'NH_3]^+N_3^-$$
$$(R' = -C_3H_7)$$

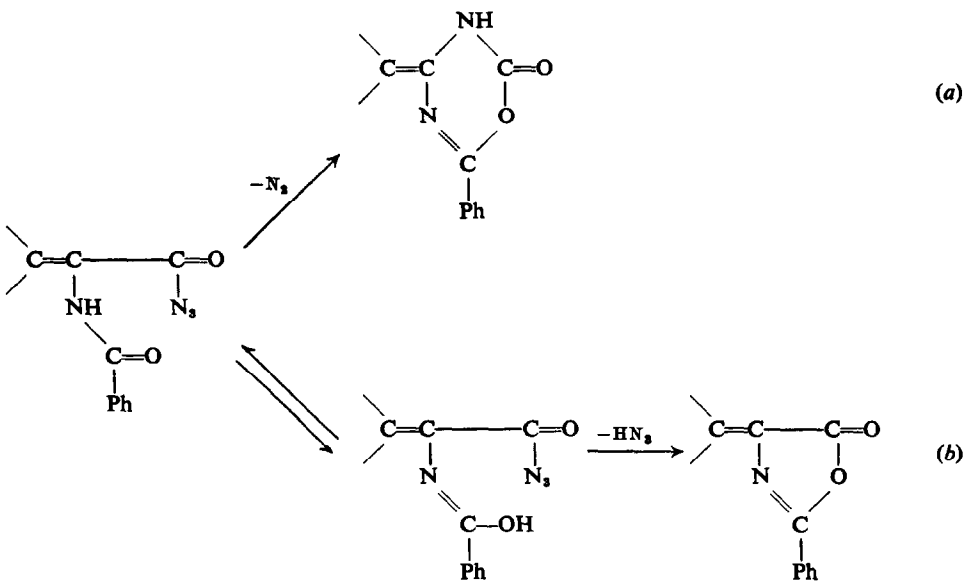
With aromatic amines (*e.g.*, aniline) nitrogen was liberated, but still the recoveries were low by 4–7%.

Decomposition in a neutral medium. When water was used as the decomposition medium, the recovery obtained was about 50%. No improvement was noticed even on increasing the boiling time up to 1 hr. If benzene or xylene was used as solvent, the recoveries obtained were high by 15–25%, corresponding to about 2·5 nitrogen atoms/azide group, instead of the expected 2 nitrogen atoms. Similarly, Smith and Hall[10] reported in their kinetic study that aryl azides decompose in decalin solution to give 1·32 mole of nitrogen instead of the expected one mole per mole of azide, but did not account for the source of the extra nitrogen. In the present work, however, the source of this extra nitrogen was found to be partial decomposition of the intermediate rearrangement product. When this product was isolated and boiled in either benzene or xylene, about 1 nitrogen atom per 2 azide groups was liberated. When the product was boiled with acetic acid no nitrogen was evolved, but ammonium acetate was detected. This can be represented as follows.



This suggested the use of acetic acid as the decomposition medium.

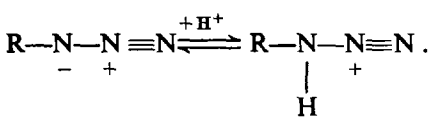
Decomposition in an acid medium. The use of dilute acetic acid (5*M*) as a decomposition medium gave invariably low recoveries varying between 83 and 90%. These low recoveries are thought to be due to the partial formation of hydrazoic acid. This assumption was tested by passing the decomposition products of isopropylidene hippuric azide through a small trap containing iron(III) nitrate solution in one experiment and silver nitrate solution in another. The formation of a deep red colour with iron(III) nitrate and a white precipitate with silver nitrate was a confirmation for this assumption.[11] Therefore, when dilute acetic acid is used, the decomposition of the azide generally proceeds *via* either of the following routes.



Route (*a*) is predominating since the average recovery is 83–90%; the remainder (*i.e.*, 10–17%) is lost owing to the formation of hydrazoic acid *via* route (*b*). When glacial acetic acid was used, the test azide compound decomposed completely *via* route (*a*).

Decomposition time

The time required for full decomposition in glacial acetic medium (*i.e.*, the time required until a constant volume of nitrogen was obtained) was recorded for the monoazide samples. The decomposition *vs.* time diagrams show that 10 min are enough for complete decomposition (*cf.* Fig. 2). The fast rate of nitrogen liberation confirms the favourable catalytic effect of the acidic medium, since the protonation of the azide group could reasonably lead to nitrogen liberation:[12]



Interferences

The nitro, nitroso, azoxy, azo, hydrazo, cyano, amido, imido, amino and ammonium compounds show no interference with the proposed procedure for azide

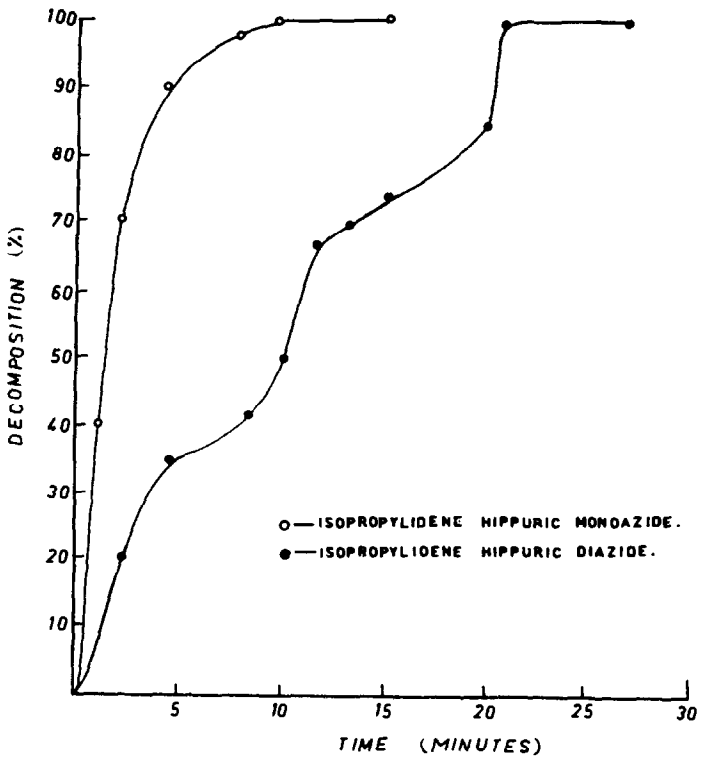


FIG. 2.—Decomposition of isopropylidene hippuric mono- and diazides in glacial acetic acid.

group determination, but diazo, diazonium and *N*-nitroso compounds seriously interfere. The first two of these interfering groups readily give off nitrogen, even on treatment with acetic acid at room temperature. The *N*-nitroso compounds (*e.g.*, cupferron) liberate nitric oxide. High recoveries were obtained for the azide group, even after the elimination of nitric oxide through oxidation with suitable reagents. The high recoveries are presumably due to gaseous products other than nitric oxide.

Determination of monoazides

Good results were obtained for the analysis of a representative series of 15 acyl azides. These azides are characterized by having an enolized γ-hydroxyl group, known to promote cyclization with subsequent loss of some hydrazoic acid,[6] and possess various substituents. The use of glacial acetic acid as a decomposition medium completely hindered this cyclization. The results obtained (Table I) show a total average recovery of 99·3% with an average absolute error of $\pm$0·13%, the maximum absolute error being $\pm$0·25%.

Determination of diazides

When diazides having both alkyl and acyl azide groups in the same molecule decompose in glacial acetic acid the nitrogen recovery corresponds approximately to one azide group; a large proportion of hydrazoic acid is also detected. This shows

TABLE I.—MICRODETERMINATION OF AZIDE GROUP IN SOME ACYL MONOAZIDES BY DECOMPOSITION IN GLACIAL ACETIC ACID

Sample	% Azide nitrogen, %		Error, %	Recovery, %
	Calc.	Found		
Benzylidene hippuric azide	9·59	9·79	+0·20	102·1
		9·76	+0·17	101·8
Isopropylidene hippuric azide	11·47	11·29	−0·18	98·4
		11·61	+0·14	101·2
Anisylidene hippuric azide	8·69	8·83	+0·14	101·6
		8·60	−0·09	99·0
Cyclohexylidene hippuric azide	9·86	9·82	−0·04	99·6
		9·65	−0·21	97·9
Piperonylidene hippuric azide	8·33	8·21	−0·12	98·6
		8·37	+0·04	100·5
Cinnamylidene hippuric azide	8·81	8·70	−0·11	98·8
		8·76	−0·05	99·4
Furfurylidene hippuric azide	9·88	9·80	−0·08	99·2
		9·69	−0·19	98·1
Isopropylidene *p*-chlorohippuric azide	10·06	9·86	−0·20	98·0
		9·90	−0·16	98·4
Isopropylidene *p*-methoxy-hippuric azide	10·22	10·35	+0·13	101·3
		10·10	−0·12	98·8
Benzylidene aceturic azide	12·17	12·31	+0·14	101·2
		12·10	−0·07	99·4
Methyl benzfurfurylidene hippuric azide	8·20	8·11	−0·09	98·9
		7·90	−0·30	96·3
Research sample 1*	8·88	8·78	−0·10	98·9
		8·80	−0·08	100·0
Research sample 2*	9·09	8·90	−0·19	97·9
		9·08	−0·01	99·9
Research sample 3*	9·15	9·11	−0·04	99·6
		9·00	−0·15	98·4
Benzoyl azide	19·05	18·82	−0·23	98·8
		18·80	−0·25	98·7

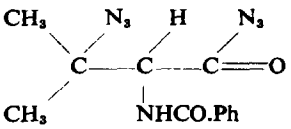
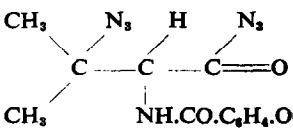
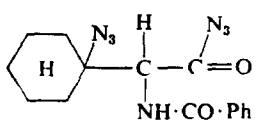
* The final structure of these samples is still under investigation but they show the characteristic band for the azide group in the infrared spectrum.

that the alkyl azide group is lost (in the form of hydrazoic acid) through decomposition, whereas the acyl azide group rearranges normally to give two-thirds of its nitrogen. It was thus thought possible to determine both nitrogen and hydrazoic acid produced from such compounds by oxidizing the hydrazoic acid quantitatively[13] in acid medium.

Recoveries corresponding to 5 nitrogen atoms/molecule of diazide were obtained when these compounds were decomposed in glacial acetic acid and the decomposition products passed through a trap containing an acidic solution of the oxidant. Both cerium(IV) sulphate and potassium permanganate were used as oxidants but the former is to be recommended. The time needed for the complete decomposition of these diazides is found to be double that required for the monoazides (*cf.* Fig. 2). Figure 2 also shows that the decomposition curve of diazides is not as smooth as that of monoazides.

More accurate results were obtained by adding one drop of the oxidant to the decomposition solution. The five nitrogen atoms obviously correspond to both the acyl azide group nitrogen (2 atoms/molecule) and that resulting from hydrazoic acid

TABLE II.—MICRODETERMINATION OF AZIDE GROUP IN SOME DIAZIDES BY DECOMPOSITION IN GLACIAL ACETIC ACID IN THE PRESENCE OF CERIUM(IV) SULPHATE

Sample	% Azide nitrogen, %		Error, %	Recovery, %
	Calc.	Found		
Isopropylidene hippuric diazide	24·46	24·70	+0·24	101·0
		24·44	−0·02	99·9
		24·82	−0·36	101·5
				
Isopropylidene anisuric hippuric diazide	22·09	22·50	+0·41	101·9
		22·44	+0·35	101·6
		22·00	−0·09	99·6
				
Cyclohexylidene hippuric diazide	21·43	21·11	−0·32	98·5
		21·88	+0·55	102·1
		21·25	−0·18	99·2
				

oxidation (3 atoms/molecule; equivalent to the alkyl azide group). The results obtained (Table II) show an average recovery of 100·6% with an average absolute error of ±0·28%, the maximum error being ±0·45%.

Zusammenfassung—Eine einfache, schnelle und genaue Mikromethode zur Analyse organischer Mono- und Diazide wird beschrieben. Sie beruht auf der Curtius-Umlagerung. Eisessig erweist sich als bestes Reaktionsmedium. Die Acylazidfunktion ergibt zwei Stickstoffatome pro Azidgruppe, die untersuchten Diazide geben jedoch letzten Endes fünf Stickstoffatome pro Gruppe, wenn man ihre Zersetzungsprodukte mit saurer Cer(IV) sulfatlösung oxidiert. Die Reaktionszeit reicht von 10 min für Monoazide bis 20 min für Diazide. Für eine typische Reine von 18 Mono- und Diaziden wurden genaue Ergebnisse erhalten.

Résumé—On décrit une microméthode simple, rapide et précise pour l'analyse des composés organiques mono-et diazides. Elle est basée sur la réaction de réarrangement de Curtius. On a trouvé que l'acide acetique cristallisable est le meilleur milieu de décomposition. La fonction acyl azide donne deux atomes d'azote par groupement azide mais les diazides étudiés en dernier donnent cinq atomes d'azote par groupe par oxydation de leurs produits de décomposition avec une solution acidifiée de sulfate de cérium(IV). Le temps de décomposition varie de 10 mn pour les monoazides à 20 mn pour les diazides. On a obtenu des résultats exacts pour une série représentative de 18 mono-et diazides.

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STUDIES ON VANADIUM(IV) COMPLEXES OF AZOXINE S DYES

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Summary—Comparative studies of the reaction of 7-arylazo-8-hydroxyquinoline-5-sulphonic acid (Azoxine S) dyes with vanadium(IV), show that 2:1 yellow, water-soluble complexes are formed over the pH range 2·5–6, and that the phenyl derivative is the most suitable for spectrophotometric determination of 0·2–1·4 ppm of vanadium(IV). The colour is formed instantaneously and is stable for about 8 hr. The molar absorptivity at λ_{max}, 400 mμ, is $1{\cdot}15 \times 10^4$, and the equilibrium constant for complex formation is of the order of 10^9. These dyes can also be used as indicators in the direct complexometric determination of vanadium(IV). The interference of a number of anions and cations is reported.

AZOXINE S (7-arylazo-8-hydroxyquinoline-5-sulphonic acid) dyes have been mainly used as metal ion indicators,[1–7] but Uusitalo and a few other workers[8–11] have carried out potentiometric and spectrophotometric studies of the complexes of bivalent metals with such dyes. In our laboratories the reactions of Azoxine S dyes with vanadium(IV) have been studied. Yellow, water-soluble, 1:2 vanadium(IV)–dye complexes are formed over the pH range 2·5–6 with all the dyes examined (Table I), but 7-phenylazo-8-hydroxyquinoline-5-sulphonic acid is the best reagent for the microdetermination of vanadium(IV). This communication reports detailed spectrophotometric studies of vanadium(IV) complexes with 7-phenylazo-8-hydroxyquinoline-5-sulphonic acid (A) and 7-(4-sulphophenylazo)-8-hydroxyquinoline-5-sulphonic acid (B).

The dyes can be used as indicators for the direct complexometric determination of vanadium(IV), the best being those derived from aniline, *o*-, *m*- and *p*-nitroanilines, *m*- and *p*-toluidines, *m*- and *p*-anisidines, *p*-phenetidine, sulphanilic acid and *p*-aminobenzoic acid. Only a few other reagents are known to perform satisfactorily in this role.[12–15]

EXPERIMENTAL

Reagents

Vanadyl solution. A solution of vanadyl sulphate in doubly-distilled water containing a small amount of sulphuric acid, was standardized with permanganate.

EDTA solution, 0·05*M*. A solution of disodium EDTA standardized against zinc solution.

Buffer solutions. Stock solutions of 1*M* sodium acetate and 1*M* acetic acid were prepared and mixed in appropriate proportions when required.

Dye solutions. All the dyes were prepared and purified by the method of Uusitalo,[8] and the purity was confirmed by elemental analysis and potentiometric titrations against standard alkali solution. The dyes were dissolved in doubly-distilled water containing the requisite amount of sodium hydroxide to effect solution. The solutions were diluted to $5{\cdot}0 \times 10^{-4}M$ for spectrophotometric studies, and used as 0·1% solutions for titrimetry.

Ionic strength. In the spectrophotometric studies an appropriate amount of potassium nitrate solution was used for maintaining constant ionic strength ($\mu = 0{\cdot}1$).

Procedure for complexometric titrations

Place an aliquot of vanadyl solution, containing 5–35 mg of vanadium, in a conical flask and buffer it to pH ~ 4, add 2 ml of 1% ascorbic acid and 2–4 drops of indicator solution. Titrate with EDTA. The end-point is marked by a sharp change in colour from green to wine-red or reddish-violet. A few results obtained with dye (A) are given in Table III.

The alternative procedure used in presence of foreign ions is as follows: take the sample solution, containing interfering ions, and add about 1 g of potassium cyanide or about 0·2 g of sodium fluoride, (depending on the nature of the ion present); this increases the pH to about 9·5. Adjust the pH with dilute sulphuric acid to ~5 and then buffer the solution to pH ~ 4. Add 5 ml of ascorbic acid solution and 4 drops of indicator and complete the titration as described above.

RESULTS AND DISCUSSION

Spectra

The absorption spectra of the dyes and vanadium complexes were measured at the optimum pH and ionic strength of 0·10; the concentrations of dye and vanadium in the final solution were both $1{\cdot}20 \times 10^{-5}M$ (Fig. 1). The results (Table I) show that (A) and (B) are superior to the other dyes studied.

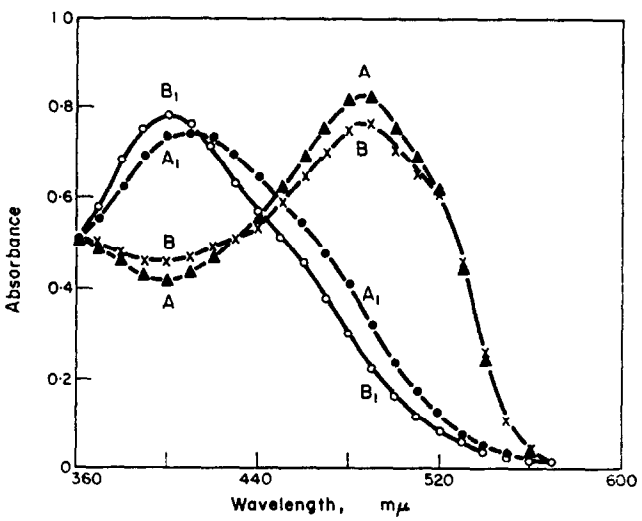


FIG. 1.—Absorption spectra for dyes (A) and (B) and their vanadium(IV) complexes. *A*—dye (A); A_1—dye (A) and vanadium(IV); *B*—dye (B); B_1—dye (B) and vanadium(IV). Final reagent concentrations were $1{\cdot}2 \times 10^{-5}M$.

Effect of pH

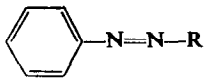
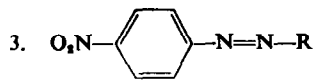
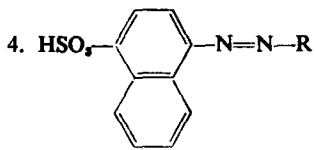
Optimum pH ranges were determined by plotting the absorbance at λ_{max} as a function of pH.

The effect of pH on the complexometric titrations was determined from titrations at different pH values with dyes (A) and (B) as indicators; the optimum pH range is 3·5–4·5.

Effect of time and temperature

The absorbance of the system was found to be constant for about 8 hr and the optimum temperature range was found to be 10–50°. It was noted that the titrations could be carried out satisfactorily over the temperature range 20–50°.

TABLE I.—PROPERTIES OF AZOXINE S DYES AND THEIR VANADIUM(IV) COMPLEXES

Dye		Absorption maxima, mμ		Colour of V(IV) complex	Optimum pH range	Optimum wavelength, mμ	Molar absorptivity at optimum wavelength		Isosbestic point, mμ
		Dye	Complex				Dye	Complex	
1. 	(A)	490	400	Yellow	3·6–4·3	400	$6·5 \times 10^3$	$11·5 \times 10^3$	443
2.	(B)	490	410	Yellow	3·7–4·3	410	$6·2 \times 10^3$	$8·5 \times 10^3$	449
3. 		490	440	Yellow	4·0–4·2	410	$8·5 \times 10^3$	$11·0 \times 10^3$	450
4. 		500	440	Yellow	3·6–4·3	420	$5·2 \times 10^3$	$7·25 \times 10^3$	470

R = 8-Hydroxyquinoline-5-sulphonic acid attached to azo group at 7 position.

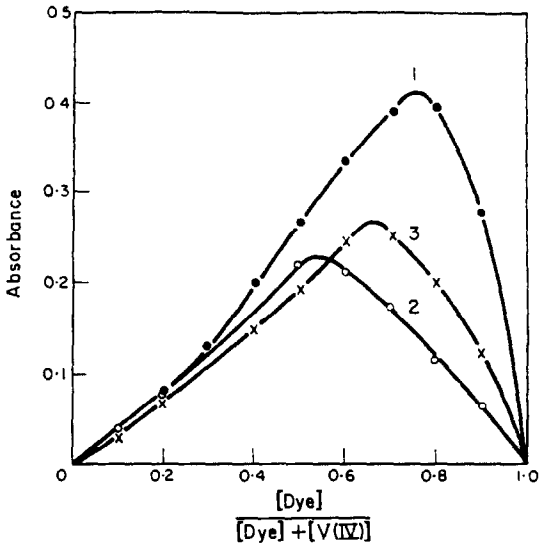


FIG. 2.—Job plots for vanadium(IV)–dye (A), at 400 mμ.
1 — $3 \times 10^{-5}M$ V(IV), 6×10^{-5} dye (A); *2* — $5 \times 10^{-5}M$ V(IV) and dye (A); *3* — $6 \times 10^{-5}M$ V(IV), $3 \times 10^{-5}M$ dye (A).

Adherence to Beer's law

Beer's law is obeyed between 0·2 and 1·4 ppm of vanadium with (A) and from 0·2 to 1·6 ppm with (B). The molar absorptivities with different dyes are given in Table I.

Nature and composition of complex

The standard spectrophotometric methods[16–19] indicated that a 1:2 metal:reagent complex was formed but no others (Figs. 2 and 3). The isosbestic points obtained for the different dyes are given in Table I. The equilibrium constants were calculated,[16,19] the results being given in Table II.

TABLE II.—EQUILIBRIUM CONSTANTS OF VANADIUM(IV) COMPLEXES WITH AZOXINE S DYES (A) AND (B) AT 25°C AND $\mu = 0{\cdot}1$

Dye used	Method*	Experimental data taken from	K	Average K
(A)	*a*	Fig. 4 curve 1	$1{\cdot}8 \times 10^9$	$1{\cdot}7 \times 10^9$
		curve 2	$1{\cdot}2 \times 10^9$	
	b	Fig. 2 curve 1	$1{\cdot}8 \times 10^9$	
		curve 2	$1{\cdot}9 \times 10^9$	
(B)	*a*	Fig. 4 curve 3	$8{\cdot}7 \times 10^9$	$7{\cdot}1 \times 10^9$
		curve 4	$7{\cdot}4 \times 10^9$	
	b	Fig. 3 curve 1	$7{\cdot}4 \times 10^9$	
		curve 2	$4{\cdot}5 \times 10^9$	

* *a* = Harvey and Manning's method.[19]
b = Job's method of non-equimolar mixtures.

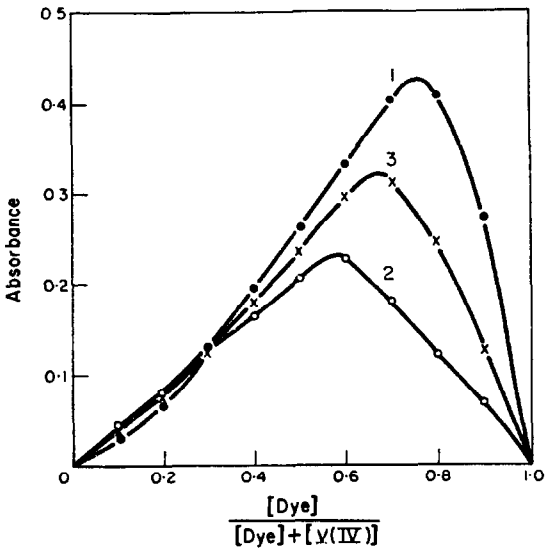


FIG. 3.—Job plots for vanadium(IV)–dye (B), at 410 mμ.
1 — 3 × $10^{-5}M$ V(IV), 6 × $10^{-5}M$ dye (B); *2* — 6 × $10^{-5}M$ V(IV) and dye (B);
3 — 6 × $10^{-5}M$ V(IV), 3 × $10^{-5}M$ dye (B).

TABLE III.—TITRATIONS OF VARIOUS QUANTITIES OF V(IV) WITH EDTA, DYE (A) BEING USED AS METAL ION INDICATOR

V(IV) taken, *mg*	EDTA required, *ml*	EDTA used, *ml*	Error, %
1·14	0·49	0·40	−18
2·28	0·97	0·95	−2
3·42	1·43	1·45	−1·5
4·56	1·94	1·95	+0·5
6·84	2·91	2·90	−0·3
11·39	4·85	4·85	0·0
15·95	6·79	6·80	+0·1
22·78	9·70	9·75	+0·5
28·47	12·10	12·00	−0·8
34·17	14·60	14·50	−0·7
45·56	19·50	19·20	−1·5
64·34	29·10	28·20	−2·8

Effect of foreign ions

The interference due to several anions and cations was studied in detail. In spectrophotometric determination of 1 ppm of vanadium(IV), double the amount of alkaline earths and 10 mg of phosphate and fluoride ions did not interfere. The interference due to equal amounts of Cu(II), Cd(II), Co(II) and Ni(II) could be avoided by masking these ions with potassium cyanide and that of Al(III), Ti(IV) and Th(IV) with sodium fluoride. However, Hg(II), Mn(II), U(VI), Fe(III), Ga(III), In(III), V(V), Mo(VI), W(VI), oxalate, tartrate and citrate ions interfered.

In complexometric titration of 22 mg of vanadium, 20 mg of alkaline earths and 100 mg of phosphate and fluoride ions did not interfere. The interference due to equal amounts of Cu(II), Cd(II), Hg(II), Mn(II), Co(II) and Ni(II) was

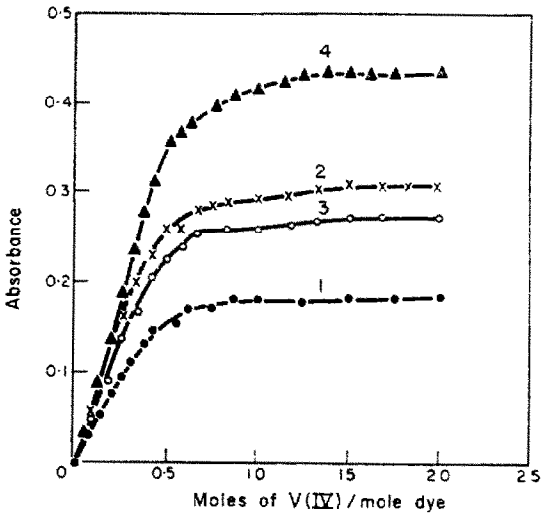


FIG. 4.—Mole-ratio curves.
1 — 4 × $10^{-5}M$ V(IV) and dye (A); *2* — 6 × $10^{-5}M$ V(IV) and dye (A);
3 — 6 × $10^{-5}M$ V(IV) and dye (B); *4* — 8 × $10^{-5}M$ V(IV) and dye (B).

overcome by masking with potassium cyanide and that of Al(III), Ti(IV) and Th(IV) with sodium fluoride. However, U(VI), Fe(III), In(III), Ga(III), Tl(III), V(V), Mo(VI), W(VI), oxalate, tartrate and citrate ions interfered in this case also.

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Zusammenfassung—Vergleichende Untersuchungen der Reaktion von 7-Arylazo-8-hydroxychinolin-5-sulfonsäure- (Azoxin S-)farbstoffen mit Vanadium(IV) zeigen, daß sich gelbe wasserlösliche 2:1-Komplexe im pH-Bereich 2,5–6 bilden und daß das Phenylderivat zur spektrophotometrischen Bestimmung von 0,2–1,4 ppm Vanadium(IV) am besten geeignet ist. Die Farbe wird sofort gebildet und ist etwa 8 Stunden stabil. Der molare Extinktionskoeffizient beim Maximum 400 nm beträgt $1{,}15 \cdot 10^4$ und die Gleichgewichtskonstante für die Komplexbildung liegt in der Größenordnung von 10^9. Diese Farbstoffe können auch als Indikatoren bei der direkten komplexometrischen Bestimmung von Vanadium(IV) verwendet werden. Über die Störung durch eine Anzahl von An- und Kationen wird berichtet.

Résumé—Des études comparatives sur la réaction de colorants acides 7-arylazo 8-hydroxyquinoléine 5-sulfoniques (Azoxine S) avec le vanadium(IV) montrent qu'il se forme des complexes jaunes 2:1, hydrosolubles, dans le domaine de pH 2,5–6 et que le dérivé phénylé convient le mieux au dosage spectrophotométrique de 0,2–1,4 p.p.m. de vanadium(IV). La coloration se forme instantanément et est stable pendant 8 h environ. L'absorption molaire à λ_{max} 400 mμ est de $1{,}15 \times 10^4$ et la constante d'équilibre pour la formation du complexe est de l'ordre de 10^9. Ces colorants peuvent aussi être utilisés comme indicateurs pour le dosage complexométrique direct du vanadium(IV). On mentionne l'interférence d'un certain nombre d'anions et de cations.

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CONTINUOUS SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF MERCURY BY RADIOACTIVE ISOTOPE-DILUTION ANALYSIS*

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Summary—The possibility of automating substoichiometric analysis by isotope dilution has been proposed previously. Automation where the analysis is based on solvent extraction has now been carried out experimentally. Preliminary experiments are described by means of which optimum conditions for this type of automated determination can be chosen and its reproducibility and selectivity checked. As an example traces of mercury down to 5×10^{-8} g are determined and the method is applied to the analysis of low-grade cinnabar ores.

IN recent years the substoichiometric determination of a number of metals by radioactive isotope dilution has been developed.[1] This method has attracted interest because though its sensitivity can be comparable with that of neutron-activation analysis, it eliminates the use of a nuclear reactor and the need for special handling facilities. In a preliminary communication,[2] the possibility of carrying out continuous substoichiometric analysis by isotope dilution was recently discussed. This procedure would have several advantages.

1. Safety precautions in a radiochemical laboratory aim to restrict radioactive contamination to a minimum. This is more easily achieved when the radioactive solutions are processed automatically by a machine.

2. In many methods of trace metal analysis the accuracy is limited at low metal concentrations (below about $10^{-6}M$) by the reproducibility of the blanks. In an automatic process every sample is treated identically so that reproducibility of blanks and calibration is guaranteed.

3. Preparation of the radioactive samples for counting is time-consuming and may lead to errors, especially when β-active samples are measured after evaporation on planchets. These difficulties are avoided in continuous analysis where flow-counters can be used.

It was pointed out[2] that continuous substoichiometry might be based on precipitation, complexation followed by ion-exchange, or solvent extraction. The present paper describes the experimental verification of the last possibility. Trace amounts of mercury have been determined by continuous isotope dilution with mercury-203, a substoichiometric amount of zinc dithizonate in carbon tetrachloride being used as the extraction reagent.

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EXPERIMENTAL

Reagents

These were prepared from analytical reagent grade chemicals.

Radioisotope. The isotope used was mercury-203, as the acetate, with a specific activity of 500 mc/g (Radiochemical Centre, Amersham, England). The material received from Amersham was diluted to give a mercury isotope solution of 500 μg/ml.

Standard labelled mercury solutions. Prepared by dilution of the mercury isotope solution with 1*M* nitric acid. Various concentrations were used according to the range of calibration required (*e.g.*, a 1-ppm standard gave a calibration graph covering the range 0·2–4·0 ppm of mercury).

Urea solutions, 1%. In water or $10^{-4}M$ sodium chloride.

Standard inactive mercury solutions. An approximately 0·05*M* solution of mercury(II) nitrate was prepared and standardized by Volhard's method.[3] This stock solution was diluted appropriately with 1*M* nitric acid.

Zinc dithizonate stock reagent. Prepared by dissolving 0·05 g of dithizone in 10 ml of ammonia solution (s.g. 0·880) and diluting to 100 ml, then extracting with carbon tetrachloride until the colour of the organic phase changed from brown to pale green. This purified aqueous solution (free from carbodiazone) was mixed with a solution of 0·05 g of zinc sulphate (heptahydrate) in 90 ml of water and 10 ml of glacial acetic acid, then extracted with 100 ml of carbon tetrachloride. The organic layer was filtered through a dry No. 41 Whatman paper and the zinc dithizonate concentration (*ca.* $5 \times 10^{-4}M$) determined (after 100-fold dilution) from its absorbance[4] at 538 mμ ($\varepsilon = 9{\cdot}2 \times 10^4$). The working solution was prepared by appropriate dilution of this stock reagent. A $2 \times 10^{-5}M$ solution is suitable for determination of mercury in the range 0·4–4 ppm.

Apparatus

Technicon AutoAnalyzer (Technicon Instruments Company Ltd., Hanworth Lane, Chertsey, Surrey, England). The system used comprised, as its main items, a two-speed proportioning pump, a sampler (Model II) and a strip-chart recorder (Bristol Dynamaster Model 570 single point, as supplied by Technicon).

Scintillation counter. The detector used was a 2 × 2 in. NaI(Tl) well-type crystal: well-diameter 1 in., volume 20 ml. This was associated with a single channel gamma-ray spectrometer (9000 Series, Research Electronics Ltd., Cleckheaton, Yorkshire, England). In all experiments a setting of discriminator voltage corresponding to 50 keV was used. This gave a background counting rate of 10 cps. The output from the ratemeter (Model 9030) was fed into the strip-chart recorder. Satisfactory results were obtained with this combination only when no earth connection was used in the recorder; otherwise the recorder pen oscillated violently. If a matched ratemeter/recorder combination is used, this difficulty should not arise.

Flow-cell. Made from 32 cm of 3·5-mm outside diameter soda glass tubing, wound into a coil, 2·2 cm in diameter and 2 cm high, which fitted into the well of our scintillation counter.

The arrangement of apparatus shown in the flow diagram (Fig. 1) resulted from all our investigations on continuous substoichiometry and was that used for the final analytical procedure. During the development of the method there was no dilution, *in situ*, of a more stable concentrated zinc dithizonate working solution with carbon tetrachloride: zinc dithizonate reagents of appropriate strength (see Figs. 2–5) were used directly.

Sampler II is programmed to deliver alternately samples (for 5 min) and 1*M* nitric acid wash-solution (for 1 min). The samples (or nitric acid wash solution) and standard labelled mercury solutions were driven by the proportioning pump (A) into the first single mixing coil (B) where isotopic exchange occurred. Urea solution, added to prevent oxidation of the organic reagent by nitrous fumes, was mixed with the solution from B in the second single mixing coil (C). The zinc dithizonate reagent was now added and this final mixture passed through the special extraction coil (D),[5] where solvent extraction took place. The two phases were separated in the electrolyte trap (E), the activity of the organic phase being continuously measured in the flow-cell (F) and recorded by the strip-chart recorder.

Development of Method

The determination of mercury with dithizone was chosen for this work because a manual substoichiometric method by isotope dilution had previously been developed.[6] Otherwise it would have been necessary, with the aid of the theory of substoichiometry,[1] to select a suitable extraction reagent and to investigate the influence of pH and time of extraction. In either case the following routine tests must be carried out whenever a substoichiometric determination by solvent extraction is being automated.

Choice of reagent concentration

The apparatus is set up as in Fig. 1 but with 1*M* nitric acid replacing the samples. During this experiment the concentration of the zinc dithizonate reagent is increased in a series of steps, from pure solvent to excess of reagent relative to the concentration of mercury in the labelled standard solution (Fig. 2).

The pumping action is started and the first level of activity registered (Fig. 2, plateau *c*) represents the quantity of mercury extracted by pure solvent. For successful substoichiometry this level must not be different from that of plateau *b*. As the concentration of reagent is increased, increasing amounts of activity are extracted (plateaux *d*, *e*, *f*, *g*) from the labelled standard solution until an

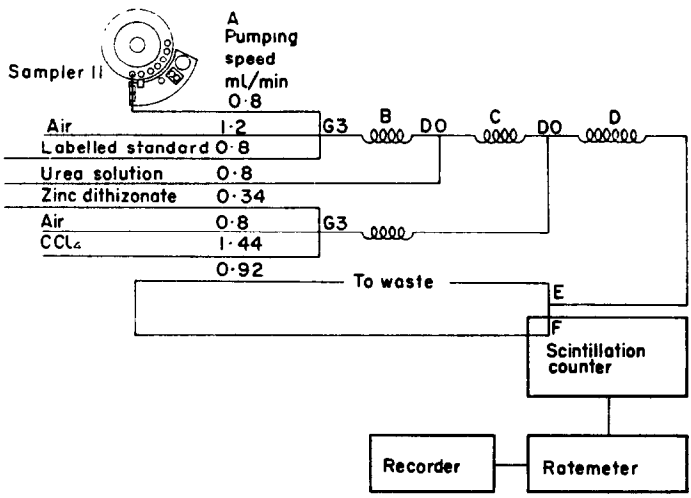

FIG. 1.—Flow diagram for continuous substoichiometric determination of mercury with the Technicon AutoAnalyzer.

excess of reagent extracts all the mercury and no further increase in activity is possible (*g*, *h*). For a substoichiometric separation any concentration of reagent could be used (*d*, *e*, *f*) which is below this limit. However, the concentration chosen (*f*) should be as high as possible so that the amount of mercury extracted minimizes statistical variations in the counting procedure. There is no need to repeat this experiment every time new reagents are prepared. The concentration of the proposed reagent should merely be checked by ensuring that it extracts less activity from the standard labelled mercury solution than is extracted by a solution of zinc dithizonate concentrated enough to give an excess of reagent with certainty.

Adsorption problems. The difference between plateaux *a* (background of the scintillation counter alone) and *b* (background of scintillation counter with flow-cell in the well), both recorded before any liquid is introduced into the apparatus, is caused by contamination of the flow cell from previous experiments. This is small for a glass flow-cell (negligible at first, but building up slowly over *ca.* 1 month, after which it is best to replace the cell and allow its activity to decay before reuse) but is important when plastic cells are used: most plastics strongly adsorb metal dithizonates (Tygon, Solvaflex, Acidflex and polythene were all useless in practice). Because of this adsorption it is necessary to use Acidflex tubing instead of the Solvaflex tubing normally recommended for pumping organic solvents (both tubings available from Technicon). Solvaflex tubing will remove all the zinc dithizonate from the reagent for several hours after pumping has started; even with Acidflex it is necessary to wait a short time (*ca.* 10 min) for adsorption losses to come to equilibrium and a constant activity to be registered. The time needed to register plateaux *a*, *b* and *c* is, however, very short (*ca.* 30 sec).

Stability of reagent

Very dilute (10^{-6} to $10^{-8}M$) solutions of organic reagents are often unstable. For automated substoichiometry the stability of such reagents is more critical than in the corresponding manual methods, because standards and samples are not processed simultaneously.

To test for reagent stability in the determination of mercury, the apparatus was arranged to deliver a substoichiometric reagent concentration. If the reagent is stable there should be no observable decrease, even after several hours, in the activity extracted. Figure 3 shows such a test with dithizone or zinc dithizonate as the extraction reagent. Clearly, zinc dithizonate is much more stable than dithizone and so it was used in all subsequent experiments.

In the present case the stability of the extraction reagent limits the sensitivity of the method and in order to determine 5×10^{-8} g of mercury it is necessary to dilute, *in situ*, a more stable concentrated zinc dithizonate working solution with carbon tetrachloride as shown in Fig. 1.

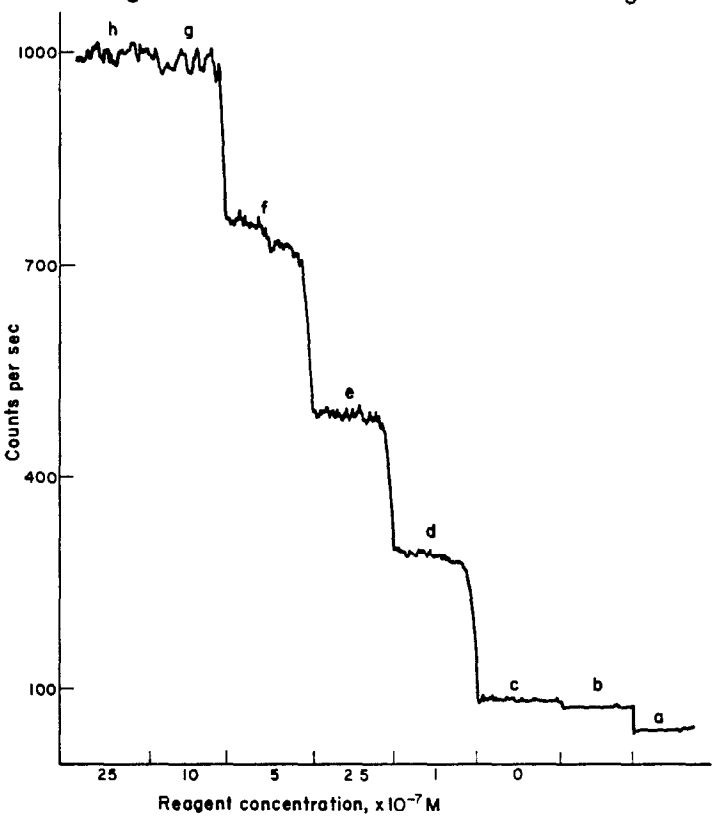

FIG. 2.—Extraction plateaux obtained with different concentrations of zinc dithizonate solution (standard labelled mercury solution: $3 \times 10^{-7}M$).

Time of extraction

It is important to check that extraction is complete in the time allowed by the AutoAnalyzer system. This is easily done by inserting a second extraction coil and seeing if there is any change in the activity extracted. It is particularly important to check this when a metal complex is used as the extraction reagent.

Choice of sampling rate

The maximum sampling rate depends primarily on the time required to replace with new solution all the old solution in the flow-cell and the electrolyte trap. This can be determined by measuring the time necessary (t_b min) for 95% of the maximum deflection to be registered on the strip-chart recorder. The maximum sampling rate is then $60/t_b$ samples/hr. For the arrangement shown in Fig. 1, t_b is 6 min, giving a maximum sampling rate of 10 samples/hr.

The sampling rate can be increased in two ways.

1. By increasing the rate at which the organic phase is pumped; however, if the sensitivity is to be maintained under such conditions, a more dilute extraction reagent would have to be used and this might be unstable. For a given sensitivity the stability of the extraction reagent limits the maximum sampling rate that can be used.

2. By reducing the size of the flow-cell, but this would reduce the counting efficiency and hence the sensitivity.

The compromise represented by Fig. 1 gives a high sensitivity but a low sampling rate.

Interferences

The effect of interferences on the extraction was investigated by using solutions of various cations (as their nitrates or sulphates), anions (as their potassium, sodium or ammonium salts) and other substances (*e.g.*, hydrogen peroxide) in the cups of Sampler II. Figure 4 shows the results of some of these studies. An interference is represented by any change in the otherwise constant activity extracted

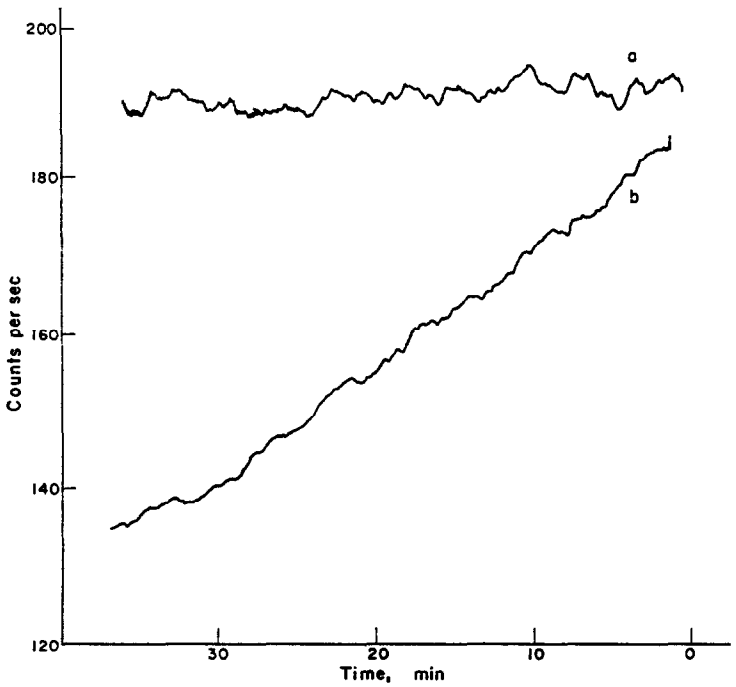

FIG. 3.—Stability of extraction reagent.
a—Zinc dithizonate ($1 \times 10^{-6}M$).
b—Dithizone (initially $2 \times 10^{-6}M$).
(Standard labelled mercury solution: $2 \times 10^{-5}M$).

from the standard labelled mercury solution (*e.g.*, palladium and chloride in Fig. 4). Table I summarizes the results for 58 ions and compounds.

It should be possible to overcome most interferences fairly easily and, for routine analysis, automatically. Cations can be masked with a suitable reagent; oxidizing and reducing agents can be destroyed with say hydrogen peroxide. Thus, silver and bismuth should be complexed with chloride and EDTA. Permanganate, dichromate and chlorate should be reduced with hydrogen peroxide or iron(II) sulphate. Tin(II), platinum(II), sulphite and hypophosphite should all be oxidized by hydrogen peroxide.

The anions in the last column of Table I present a more serious difficulty, particularly chloride, which is almost impossible to remove at the very low concentrations where interference is still encountered (calculated to be down to about 0·001 ppm). These anions appear to form ternary complexes of the type Cl·Hg·HDz' (H_2Dz = dithizone) so that a given amount of zinc dithizonate could extract twice as much mercury from solutions containing them as from solutions in which mercury is extracted as the primary dithizonate, $Hg(HDz)_2$. This will lead to an increase in the activity extracted, in contrast with other interferences (*e.g.*, palladium in Fig. 4) which cause a decrease.

It can be predicted theoretically that interference from chloride will be overcome if its concentration is between 6×10^{-5} and $6 \times 10^{-3}M$, under which condition all mercury is present as mercury(II) chloride. This has been confirmed experimentally and we recommend the use under all circumstances

of a 1% urea solution in $10^{-4}M$ sodium chloride. This method is, of course, only satisfactory if an empirical calibration graph is constructed. The chemistry of the reactions is being investigated more fully and will be reported at a later date.

Calibration graph

The calibration graph (Fig. 5) was prepared by using standard inactive mercury solutions in the cups of Sampler II. A fresh calibration graph should be prepared whenever new reagents are made up, particularly when the method given above to overcome interference from chloride is used. If a very large amount (*ca.* $1M$) of bisulphate or nitrate is present, a similar amount should be added to the standard inactive mercury solution to compensate for their small but noticeable interference.

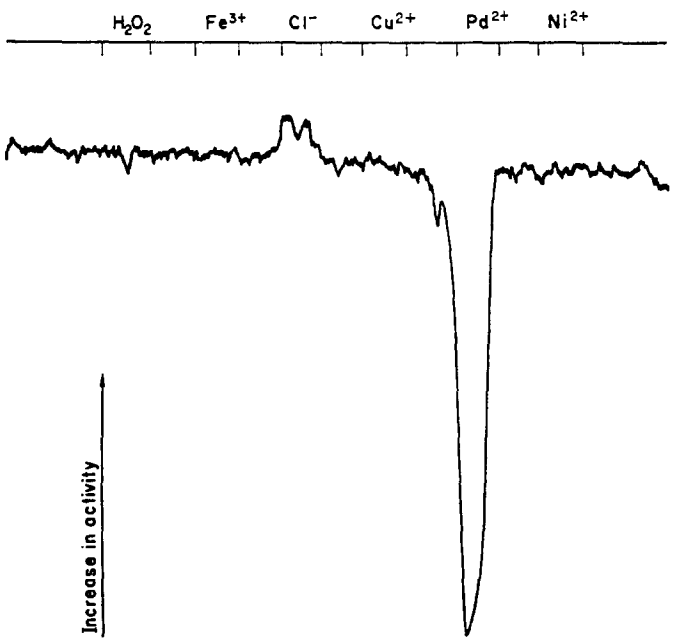

FIG. 4.—Effect of foreign ions (conditions as detailed in Table I).

As can be seen from Fig. 5, as little as $2{\cdot}5 \times 10^{-7}$ g of mercury in 5 ml of solution (0·05 ppm) can be determined (in a 6-min run 4·8 ml of sample solution are consumed). The lowest amount of mercury we have determined by this method is 5×10^{-8} g in 5 ml (0·01 ppm).

Analysis of Test Samples

In order to demonstrate the usefulness of the method, we analysed several samples of low-grade cinnabar ore which had previously been analysed spectrophotometrically for mercury at the Warren Spring Laboratory.

One g of ore (received as fine powder and used directly) was refluxed for 30 min with 25 ml of sulphuric acid (s.g. 1·84) and 1 g of potassium nitrate. After cooling and dilution, 1 g of urea was added, the mixture filtered through a No. 42 Whatman paper, and the filtrate diluted to 250 ml in a calibrated flask.

The solution was analysed with the apparatus as shown in Fig. 1, using the following solutions: standard labelled mercury solution—$5 \times 10^{-6}M$; urea solution—1% in $10^{-4}M$ sodium chloride; zinc dithizonate working solution—$5 \times 10^{-6}M$. The AutoAnalyzer was run at a rate of 5 samples/hr, and gave the results shown in Table II.

DISCUSSION

Our results for the determination of mercury in the low-grade cinnabar ores (Table II) by continuous substoichiometry are in good agreement with the spectrophotometric results, though for Sample 3 there was disagreement with the spectrophotometric values reported by Warren Spring Laboratory. For the determination

TABLE I.—STUDY OF INTERFERENCES*†

Substances which do not interfere at a concentration of 1000 ppm	Metals which interfere by competing with mercury for the zinc dithizonate	Ions which interfere by oxidizing zinc dithizonate	Substances which interfere by complexing mercury	Ions which interfere by reducing mercury to metal	Anions which interfere by forming ternary complexes
NH_4^+ Se^{4+} SO_4^{2-}	Au^{3+}	MnO_4^-	CN^-¶	Sn^{2+}¶	Cl^-
K^+ Te^{4+} ClO_4^{2-}	Pd^{2+}	$Cr_2O_7^{2-}$	SCN^-	$N_2H_5^+$‡	Br^-
Na^+ Tl^+ Acetate	Pt^{2+}	NO_2^-	I^-		HPO_3^-
Mg^{2+} Cr^{3+} Citrate	Pt^{4+}‡	ClO_3^-‡‡	SO_3^{2-}		HSO_4^-**
Ca^{2+} Mn^{2+} Tartrate	Ag^+‡	Ce^{4+}¶	$S_2O_3^{2-}$¶		NO_3^-††
Ba^{2+} Fe^{2+} Oxalate	Bi^{3+}‡		F^-¶		
Al^{3+} Fe^{3+} Borate			EDTA‡		
Ga^{3+} Co^{2+} Molybdate					
In^{3+} Ni^{2+} $S_2O_8^{2-}$					
Ce^{3+} Cu^{2+} H_3PO_4					
Th^{4+} Zn^{2+} H_2O_2					
Sb^{3+} Pb^{2+}					
As^{3+} Be^{2+}					

* Standard labelled mercury solution: $2{\cdot}5 \times 10^{-6}M$; zinc dithizonate working solution: $5 \times 10^{-7}M$; acidity $1N$ in HNO_3 (chosen so as to overcome the known interference from Bi^{3+} and Cu^{2+}) except during the examination of H_2SO_4 and HNO_3 when the total acidity varied from 0·01 to $10N$.

† Any ion or substance changing the activity extracted by more than 1% is assumed to interfere; concentrations down to 0·1 ppm or less interfere unless stated otherwise.

‡ Interferes if present in excess of 100 ppm.

¶ Investigated only at 1000 ppm.

** Interferes if present in excess of $0{\cdot}05M$.

†† Interferes if present in excess of $0{\cdot}5M$; interference from using $1M$ HNO_3 as a working medium can be compensated for by adding it to the standards used for calibration.

‡‡ Interferes if present in excess of 10 ppm.

of traces of mercury with dithizone, continuous substoichiometry is more sensitive by an order of magnitude than spectrophotometry as judged by comparing Fig. 5 with spectrophotometric data.[8]

The advantages of the automatic method mentioned earlier should be weighed against the disadvantages which are now evident. First, there is a slow contamination of parts of the instrument (tubing, nipples, glass coils, *etc.*) by adsorption of radiomercury. Secondly, the automatic method is less sensitive than manual substoichiometry (by about one order of magnitude in the case of mercury) because the flow-cell is small and the organic phase passes rapidly through it. Fortunately radioisotopes of other metals are available with higher specific activities than that of mercury-203, many of them as carrier-free isotopes. This should permit determination of these metals at even lower concentrations than in the case of mercury.

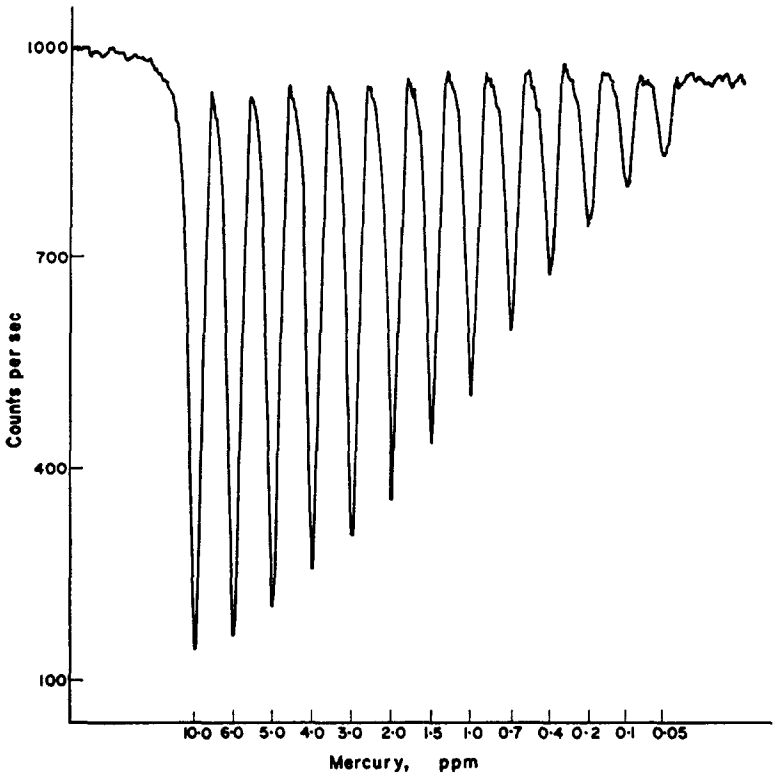

Fig. 5.—Calibration graph for determination of mercury (standard labelled mercury solution: $5 \times 10^{-6}M$; zinc dithizonate solution: $7 \times 10^{-7}M$).

Table II.—Analysis of low-grade cinnabar ores*

Method of analysis	Mercury, %			
	Sample 1	Sample 2	Sample 3	Sample 4
Continuous substoichiometry†	0·017	0·064	0·069	0·030
Spectrophotometry in this laboratory†‡	0·021	0·071	0·066	0·036
Spectrophotometry at Warren Spring Laboratory¶	0·020	0·068	0·045	0·033

* Provided by Dr. P. G. Jeffery, Warren Spring Laboratory, Ministry of Technology, Stevenage, Herts., England.
† Results are the average of duplicate analyses.
‡ Using the Unicam SP600 and dithizone; sample dissolution as for continuous substoichiometry.
¶ Using dithizone screened with EDTA and KSCN; sample dissolution as for continuous substoichiometry.

Because the volume which can be sampled by the AutoAnalyzer is small (maximum of 10 ml), an increase in sensitivity by increasing the sample volume would entail a preliminary extraction. However, this disadvantage could be outweighed by introduction of the radioisotope before the preliminary extraction. Because isotope-dilution analysis is being used, this preliminary separation need not then be quantitative. As the radioisotope is not being introduced into the AutoAnalyzer continuously, the strip-chart records and their evaluation would differ from those discussed above.

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Zusammenfassung—Vor kurzem wurde die Möglichkeit angegeben, die unterstochiometrische Analysenmethode durch Isotopenverdünnung zu automatisieren. Bei einer auf flüssig-flüssig-Extraktion beruhenden Analyse wurde die Automation jetzt experimentell verifiziert. Es werden Vorversuche angegeben, durch die die optimalen Bedingungen für diese Art automatischer Analyse ausgewählt und deren Reproduzierbarkeit und Selektivität geprüft werden können. Als Beispiel werden Quecksilbermengen bis herunter zu 5×10^{-8} g bestimmt und die Methode auf die Analyse geringwertiger Zinnober-Erze angewandt.

Résumé—On a proposé antérieurement la possibilité d'automatiser l'analyse substoechiométrique par dilution isotopique. On a maintenant réalisé expérimentalement l'automatisation pour les cas où l'analyse est basée sur une extraction par solvant. On décrit des expériences préliminaires au moyen desquelles on peut choisir les conditions optimales pour ce type de détermination automatisée et vérifier la reproductibilité et la sélectivité. A titre d'exemple, on dose des traces de mercure pouvant descendre jusqu'à 5×10^{-8} g et applique la méthode à l'analyse de minerais de cinabre pauvres.

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STUDIES IN ATOMIC-FLUORESCENCE SPECTROSCOPY—VI*

THE FLUORESCENCE CHARACTERISTICS AND ANALYTICAL DETERMINATION OF BISMUTH WITH AN IODINE ELECTRODELESS DISCHARGE TUBE AS SOURCE

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Summary—The atomic-fluorescence characteristics of bismuth atoms in cool nitrogen–hydrogen and argon–hydrogen diffusion flames burning in air are described. Excitation is obtained from the non-resonance iodine line at 2061·63 Å emitted by a microwave-excited electrodeless discharge tube operating at 2450 Mc/s. Fluorescence of the bismuth resonance line at 2061·70 Å is observed and also direct-line fluorescence at 2697 and 3025 Å. In addition thirteen other much weaker lines were observed and two unidentified lines at 2880 and 2680 Å. The emissions at 2628 and 2938 Å appear to arise from "thermally assisted direct line fluorescence". The most intense line at 3025 Å permits linear-dependence analytical atomic-fluorescence measurements to be made in the range 0·1–200 ppm with a detection limit of 0·05 ppm and with no problems of source scatter. No interference was observed from hundred-fold concentrations of fourteen ions. Matrix effects from aluminium and magnesium were overcome by raising the temperature of the cool diffusion flames. A bismuth microwave-excited electrodeless discharge tube was used as a source for atomic-absorption measurement in air–hydrogen and air–propane flames at 2231 Å with a detection limit of 1 ppm and a linear-dependence analytical range of 10–100 ppm. With the iodine microwave-excited electrodeless discharge tube the detection limit for atomic absorption was 10 ppm at 2062 Å.

THE determination of bismuth by flame emission spectrophotometry is difficult because the main resonance line at 3068 Å lies in the middle of the hydroxyl band emission region and hence excessive background radiation is present. In addition, Gilbert[1] has noted absorption by bismuth atoms of the radiation from a hydroxyl band at 3068 Å in an oxy-hydrogen flame, thereby introducing more problems. The other bismuth resonance lines lie in the far ultraviolet and are in consequence difficult to excite thermally. At present, the most sensitive emission studies have been made in the inner cone of an oxy-acetylene flame in conjunction with nebulized organic solvents. Dean[2] gives a limit of detection of 6·4 ppm for bismuth under these most favourable conditions at 2231 Å.

Atomic-absorption measurements have been made at 3068 Å by Gatehouse and Willis,[3] who used a hollow-cathode lamp giving a limit of detection of 2 ppm. They stated that a line at 2320 Å, which we have been unable to detect, gave the strongest absorption, but because of the nearness of another line (at 2319·8 Å, which they attributed to nickel) the calibration curve became flattened above 50 ppm. This is a

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direct consequence of the low intensity output of some hollow-cathode lamps. A similar observation on the use of a conventional hollow-cathode lamp for iron has been made recently by Marshall and West.[4] Absorption studies have also been made with the continuum from a hydrogen lamp as source and with photographic recording of line intensities.[5] The integrated limits of detection in this instance were estimated to be 0·5–1·0 ppm for the 2062, 2231 and 3068 Å lines and 4·0 ppm for the 2228 Å line.

This communication deals with further developments in atomic-fluorescence spectroscopy and the use of microwave-excited electrodeless discharge tubes as spectral sources for atomic-absorption as well as atomic-fluorescence. It also describes the use of cool diffusion flames as atom reservoirs for atomic-fluorescence spectroscopy.

In this investigation the bismuth atoms were excited by the iodine line at 2061·63 Å (corresponding to the $5s^25p^4\ ^3P_2s \rightarrow 5s^25p^5\ ^2P^0_{1/2}$ transition)[6] from an iodine electrodeless discharge tube. This iodine line, which coincides almost exactly with a bismuth resonance line at 2061·70 Å (corresponding to the $^4P_{2\frac{1}{2}} \rightarrow {}^4S^0_{1\frac{1}{2}}$ transition), results from a non-ground-state transition and is hence not subject to self-reversal effects, even when the source is operated at high power ratings. In addition, an iodine discharge tube is as stable and easy to operate as that of an inert gas such as argon. Moreover, the iodine discharge tube does not emit radiation which is concident with the direct-line fluorescence signal from the bismuth atoms at 3025 Å and so scattering from the source is completely eliminated. This latter consideration is of considerable importance because scattering is potentially one of the most serious limitations in atomic-fluorescence spectroscopy. We have not found this to be so in practice.

EXPERIMENTAL

Preparation of electrodeless discharge tubes

Iodine. Quartz tubes between 6 and 7 cm in length and 8 mm internal diameter were prepared as described in previous communications.[7,8,9] The empty tube was heated to red heat with an oxy-propane blow torch and subjected to evacuation for about 10 min. During this time, argon was periodically flushed through the system to sweep away any impurities desorbed from the walls of the tube. After cooling under vacuum, the tube was removed from the vacuum line and a small amount (*ca.* 10 mg) of iodine was added. The tube was then evacuated and as much of it as possible was immersed in a beaker of water at *ca.* 40°. The system was flushed three times with argon to remove any occluded gases or moisture in the iodine. The iodine should not be heated directly with a flame because of its volatility. The tube was finally sealed under an argon pressure of *ca.* 1 mm Hg.

Bismuth. These tubes were prepared in a manner exactly similar to that described previously for antimony,[9] *i.e.*, with *ca.* 10 mg each of bismuth and iodine. A tube 3–4 cm in length, sealed under a final argon pressure of 1·0 mm Hg was found to be most suitable. Tubes containing only bismuth metal were not used, because of its involatility.

Spectral characteristics of discharge tubes

Iodine. These tubes were operated on the lower (0–25 W) range of the generator at 12–15 W with the upper portion of the tube within the cavity. The most stable and intense discharge was obtained by strongly cooling the lower portion (*ca.* 4 cm) of the tube protruding below the cavity, with a stream of air from a compressor. This prevents an undue increase in the vapour pressure of iodine and consequent unstable emission.

The only iodine line observed was the extremely intense one due to the $5s^25p^4\ ^3P_2s \rightarrow 5s^25p^5\ ^2P^0_{1\frac{1}{2}}$ transition at 2061·63 Å *cf.* Fig. 1. The remainder of the spectrum was a broad, low intensity, continuum extending from *ca.* 2400 Å into the visible region. Under optimized conditions of tuning and cooling, the iodine discharge occupied about two-thirds of the tube and in a period of over an hour showed a 1% maximum variation in response (see Fig. 1).

Bismuth. A stable, but low intensity, discharge was obtained by operating the tube at 40 W with only slight cooling. Under these conditions all the spectral lines shown in the Grotrian diagram given by Candler[6] were observed. In addition, a line at 2228 Å, not shown by Candler, was also observed

This line is, however, recorded by Brode[10] and it can be predicted indirectly from the energy difference between the $^4S_{1\frac{1}{2}}$ and $^4P_{1\frac{1}{2}}$ states. It has also been used elsewhere in the atomic-absorption of bismuth.[5] The low intensity of the observed lines is thought to be due to the involatility of bismuth tri-iodide (m.p. 409°). The intensity increased at higher operating power (60–70 W) and the colour of the discharge changed from red-pink to white-blue. An even brighter discharge was obtained without cooling, but under these conditions the tubes became overheated, with eventual loss of stability. The most intense emission obtained in all the various types of discharge was at 3068 Å.

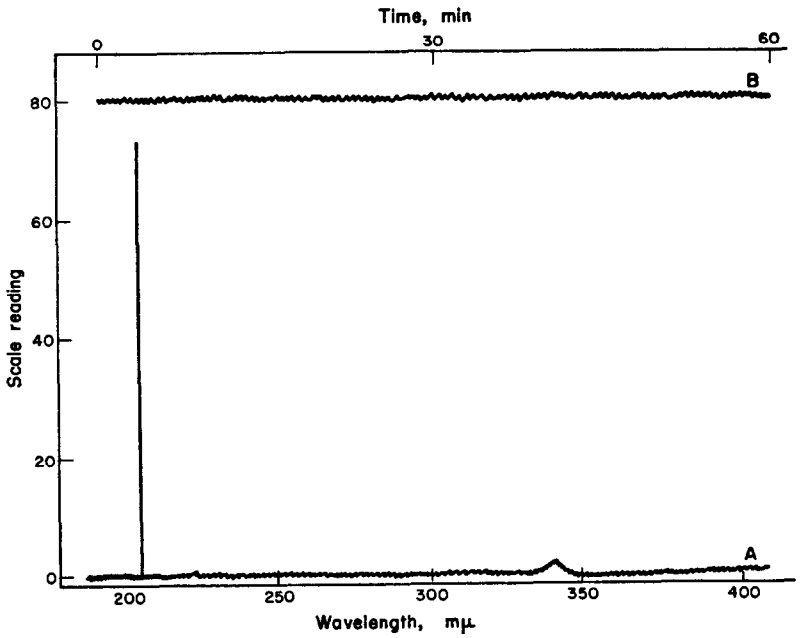

FIG. 1.—(A) Emission spectrum of iodine microwave-excited electrodeless discharge tube at 2450 Mc/s and 12 W.
(B) Stability plot of iodine tube at 2062 Å.

Atomic-fluorescence measurements

Source. The bismuth discharge tubes were examined as sources of excitation, but they were found to be either of rather low intensity or else somewhat unstable. Also, the most intense resonance line present in the discharge, at 3067·72 Å, coincides with a hydroxyl band emission from the flame in this region. In our arrangement[11] both the flame background and fluorescence emission signals are amplified by the a.c. detection system of the Unicam 900A because the source is not modulated. However, even with modulation it would be unwise to measure at this wavelength (*i.e.*, 3067·72 Å) because of variations in the intense flame background.

In consequence, the iodine discharge tube was selected as the most suitable source of excitation because the extremely intense non-resonance iodine line emission at 2061·63 Å is sufficiently close to the 2061·70 Å bismuth resonance line for some absorption by bismuth atoms to occur. The cross-matching of iodine and bismuth spectra does not appear to have been reported previously in the literature, although many instances are known to exist between iron and other elements.[12]

Another unreported instance of cross-matching which we have recently noted in these studies is that between the non-resonance line of arsenic at 2288·12 Å and the cadmium resonance line at 2288·02 Å. It is possible that many other instances exist which can be used with advantage, particularly in atomic-fluorescence spectroscopy, where it is not necessary to have the absorption line profile completely encompass the source line. Under these conditions absorption of the iodine line at 2062 Å would be expected with fluorescence emission from the bismuth resonance line at 2062 Å and direct-line emission at 2697 and 3025 Å.

Flame. Because of its low background a special type of diffusion flame, which has been fairly fully discussed by us elsewhere[13] in a communication concerned with molecular emission spectroscopy in cool flames, was used in these studies. These cool diffusion flames have several advantages over

the hot premixed flames commonly used in atomic-absorption spectroscopy. For comparison, a $10^{-3}M$ solution of bismuth nitrate was nebulized into low background flames and the fluorescence emission was measured at 3025 Å (see below): the flames used were air–propane and air–hydrogen premixed flames and nitrogen–hydrogen and argon–hydrogen diffusion flames. The diffusion flames were obtained with the same burner-head and gas jets as used for the air–hydrogen flame, and the nitrogen or argon was used as the nebulizing gas.

The optimized fluorescence signal was exactly the same in the two premixed flames and in the nitrogen–hydrogen diffusion flame, but was twice as large in the argon–hydrogen diffusion flame. We attribute this difference to the fact that in a collisional encounter the diatomic nitrogen molecules would be expected to absorb energy from the excited bismuth atoms more efficiently than argon atoms, *i.e.*, they would exhibit greater quenching action. The rate of sample uptake was similar (±1%) for all gases and was 1·72 ml/min.

Although diffusion flames are very cool[13] in comparison with the premixed flames which are normally used in thermal-emission and atomic-absorption spectroscopy, and may in consequence be more prone to show matrix effects, they also have considerable advantages. For example, the air–ground radiation propane flame back at 3025 Å is *ca.* 100 times as high as that of the diffusion flames; that of the air–hydrogen flame is *ca.* 25 times as high. This permits lower limits of detection and increased precision in both atomic-absorption and atomic-fluorescence spectroscopy. Because of the low temperatures of diffusion flames, thermal-emission from the alkali and alkaline earth elements is considerably reduced. In the atomic-fluorescence of bismuth no interference was observed from a 100-fold molar excess of sodium and potassium (see below) in a diffusion flame. The transparency of these flames is also of very great significance, especially when dealing with elements which have resonance lines in the far ultraviolet region of the spectrum, *e.g.*, arsenic.[14] This again results in a considerable lowering of detection limits and often a much wider working range becomes available. This is particularly important if an inefficient source is used, *e.g.*, a conventional arsenic hollow-cathode lamp.

Wavelength of measurement. A 200-ppm bismuth solution was nebulized with argon into an argon–hydrogen diffusion flame which was irradiated by an iodine electrodeless discharge tube. The essential optimum conditions of operation were found to be: hydrogen pressure corresponding to a reading of 16 cm on a di-n-butyl phthalate manometer gauge (flame near lift-off point); argon pressure 15 psi; top of the burner head *ca.* 3 cm below the bottom of the analysing monochromator slit. The fluorescence response was found to be rather dependent on the hydrogen pressure and burner head height. Optimized signals were obtained with a hydrogen pressure slightly more than sufficient to prevent flame lift-off and with fluorescence measurements made half way up the flame. The most intense fluorescence signals obtained under these conditions are shown in Table I. A comparison is also made with the less sensitive nitrogen–hydrogen diffusion flame.

TABLE I.—MAJOR ATOMIC-FLUORESCENCE WAVELENGTHS

Spectral line, Å	Fluorescence transition	Slitwidth, mm	Relative fluorescence signal*	
			N_2/H_2	Ar/H_2
2062	$^4P_{2\frac{1}{2}} \rightarrow {}^4S_{1\frac{1}{2}}{}^0$	0·017	6·5	12
2697	$^4P_{2\frac{1}{2}} \rightarrow {}^2D_{1\frac{1}{2}}{}^0$	0·017	3	6
3025	$^4P_{2\frac{1}{2}} \rightarrow {}^2D_{2\frac{1}{2}}{}^0$	0·017	50	100
3068	$^4P_{\frac{1}{2}} \rightarrow {}^4S_{1\frac{1}{2}}{}^0$	0·017	28	54

* Identical gain for both flames.

As expected, the three fluorescence signals were obtained from the $^4P_{2\frac{1}{2}}$ state. The additional intense signal at 3068 Å must be due to deactivation of the excited $^4P_{2\frac{1}{2}}$ state atom by radiationless transitions to the $^4P_{\frac{1}{2}}$ excited state. The high intensity of the emission at 3068 Å arises because the $^4P_{\frac{1}{2}}$ is the lowest lying excited state and it may be populated by radiationless transfers from other excited states. Moreover, it is the only line other than the 4722 Å ($^4P_{\frac{1}{2}} \rightarrow {}^2D_{1\frac{1}{2}}{}^0$ transition), which can be emitted from this state. The analogous behaviour of the $^3P_1{}^0 \rightarrow {}^1S_0$, 2537 Å mercury line can be explained similarly.

In addition to the more intense fluorescence signals shown in Table I, many unexpected and much weaker signals were recorded. These are shown in Table II and are compared to the weakest signal shown in Table I (at 2697 Å), *cf.* Fig. 2. The two lines at 2989 and 2993 Å could not be resolved at the slitwidths used. In addition to these emissions, two unidentified peaks were obtained at 2880 and

TABLE II.—MINOR ATOMIC-FLUORESCENCE WAVELENGTHS

Spectral line, Å	Transition	Relative fluorescence signal N_2/H_2*	Relative fluorescence signal Ar/H_2†
2697	$^4P_{2\frac{1}{2}} \rightarrow {}^2D_{1\frac{1}{2}}{}^0$	100	100
2628	$^2P_{1\frac{1}{2}} \rightarrow {}^2D_{1\frac{1}{2}}{}^0$	7	12
2938	$^2P_{1\frac{1}{2}} \rightarrow {}^2D_{2\frac{1}{2}}{}^0$	30	47
2898	$^2P_{\frac{1}{2}} \rightarrow {}^2D_{1\frac{1}{2}}{}^0$	61	90
4122	$^2P_{\frac{1}{2}} \rightarrow {}^2P_{\frac{1}{2}}{}^0$	11	17
2228	$^4P_{1\frac{1}{2}} \rightarrow {}^4S_{1\frac{1}{2}}{}^0$	17	21
2989	$^4P_{1\frac{1}{2}} \rightarrow {}^2D_{1\frac{1}{2}}{}^0$	32	42
3397	$^4P_{1\frac{1}{2}} \rightarrow {}^2D_{2\frac{1}{2}}{}^0$	11	17
2231	$^2D_{2\frac{1}{2}} \rightarrow {}^4S_{1\frac{1}{2}}{}^0$	34	44
2277	$^2D_{1\frac{1}{2}} \rightarrow {}^4S_{1\frac{1}{2}}{}^0$	5·5	9
2993	$^2D_{2\frac{1}{2}} \rightarrow {}^2D_{1\frac{1}{2}}{}^0$	32	42
3511	$^2D_{1\frac{1}{2}} \rightarrow {}^2D_{2\frac{1}{2}}{}^0$	6·5	11
4722($6s^26p^27s$)	$^4P_{\frac{1}{2}} \rightarrow {}^2D_{1\frac{1}{2}}{}^0$	47	49
2781($6s^26p^28s$)	$^4P_{\frac{1}{2}} \rightarrow {}^2D_{1\frac{1}{2}}{}^0$	4	6·5

* Slitwidth 0·06 mm.
† Slitwidth 0·04 mm. Gain adjusted to give 100 divisions scale reading at 2697 Å in each flame.

2680 Å, and with an increased gain and slitwidth a slight fluorescence signal was obtained at 2110 Å, corresponding to the $6s^26p^28s\ ^4P_{\frac{1}{2}} \rightarrow {}^4S_{1\frac{1}{2}}{}^0$ transition. The 1954, 1959, 2524 and 2810 Å lines from the $6s^26p^27d\ ^2D$ states lie *ca.* 0·3 eV above the $^4P_{2\frac{1}{2}}$ and could not be detected. Also no fluorescence signal was observed from the 2021 Å line ($^2P_{1\frac{1}{2}} \rightarrow {}^4S_{1\frac{1}{2}}$ transition), but this is a very low intensity transition and lies at a wavelength at which the sensitivity of the photomultiplier becomes vanishingly small.

Table I indicates that the ground state bismuth atom can absorb energy from the iodine discharge tube at 2062 Å, be excited to the $^4P_{2\frac{1}{2}}$ state and then give rise to resonance fluorescence at 2062 Å,

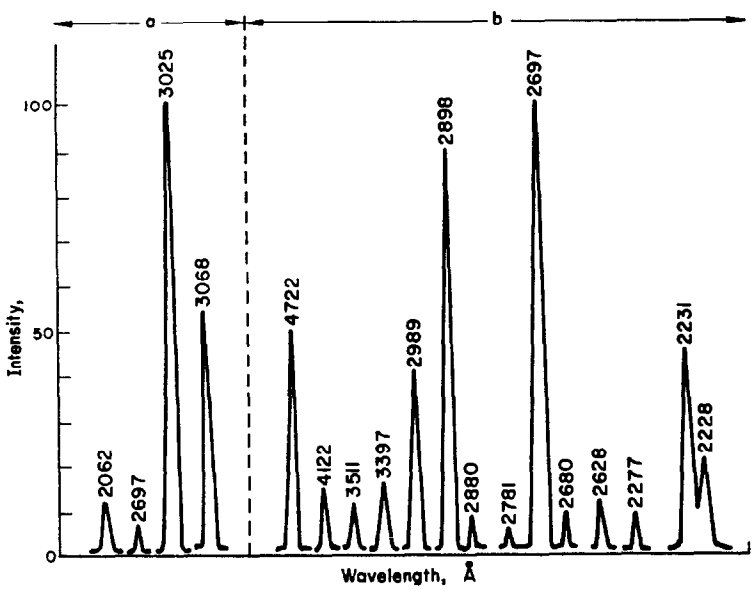

FIG. 2.—Fluorescence emission spectra of bismuth in the argon–hydrogen diffusion flame with iodine microwave tube as source.
(*a*) *cf.* Table I; (*b*) *cf.* Table II.

direct-line fluorescence at 2697 and 3025 Å and multiple stepwise fluorescence at 3068 Å. Although the absolute intensities of these lines vary in the two flames examined, their ratio is constant. This is to be expected because quenching of an excited state should not alter the ratio of line intensities emitted from that state. This effect is again observed for other states shown in Table II.

It is apparent from Tables I and II that not only are the readings obtained in the argon–hydrogen diffusion flame greater than those in the nitrogen–hydrogen diffusion flame under similar conditions, but that the ratio of a given line intensity to the 2697 Å line in the same flame is in general 50% more in the argon–hydrogen flame, for reasons which have already been explained. The fluorescence emissions shown in Table II are of no real analytical significance because their intensity is rather low, but they do give a good indication of the population of the various energy levels. The fluorescence emissions at 2628 and 2938 Å which originate from the $^3P_{1\frac{1}{2}}$ state are examples of *thermally assisted* direct-line fluorescence, which was first postulated in our previous communication on the atomic fluorescence characteristics of antimony.[9] In this instance there must be a radiationless promotion from the $^4P_{2\frac{1}{2}}$ to the $^3P_{1\frac{1}{2}}$ state (energy difference of only 0·12 eV). The other fluorescence emissions shown in Table II may be attributed to stepwise and/or direct-line fluorescence.

TABLE III.—ATOMIC-ABSORPTION MEASUREMENTS
(100 ppm OF BISMUTH)

Spectral line, *Å*	Slitwidth, *mm*	Absorbance
3068	0·003	0·130
2231	0·015	0·348
2228	0·018	0·162
2277	0·020	0·025
2062	0·001	0·028
3025	0·010	0·000

All the fluorescence signals obtained can be attributed to the initial absorption of the 2061·63 Å iodine line. This was verified by the introduction of suitable filters. For example, a 10% solution of acetone in distilled water, contained in a quartz cuvette (1-cm path length) and placed between the monochromator slit and the iodine source, shows complete absorption between 2220 and 3000 Å, with 23·5% and 3% transmittance at 2062 and 3025 Å respectively. These transmission readings are uncorrected for reflection and absorption by the walls of the quartz cuvette. When this filter was interposed between the source of excitation and the flame, the fluorescence signal at 3025 Å decreased from 100 to 24 divisions on the scale. This decrease corresponds almost exactly to the extent of the absorption of the 2061·63 Å iodine line by the acetone filter. Similarly a 0·1*M* nickel chloride filter gave 6 and 80% transmittance at 2062 and 3025 Å respectively. When this filter was placed between the source and flame, the fluorescence signal at 3025 Å decreased from 100 to 6 divisions. This again corresponds to the absorption of the 2061·63 Å iodine line by the filter. Finally, a Pyrex glass filter gave 0 and 50% transmittance at 2062 and 3025 Å and when placed between source and flame produced a fluorescence signal decrease at 3025 Å from 400 divisions to 1. These results prove conclusively that the initial absorption step in the whole fluorescence process is absorption of the 2061·63 Å iodine line.

The 3025 Å line exhibits the greatest sensitivity and there is negligible scattering from the source at this wavelength. Linear calibration curves have been obtained at 3025 Å over the range from $5 \times 10^{-7}M$ to $10^{-3}M$ solutions of bismuth (0·1–200 ppm) and the slope of the log-log curve was 0·93. The limit of detection (signal:noise ratio of 1) in aqueous solution was $2·5 \times 10^{-7}M$, *i.e.*, 0·05 ppm of bismuth, with a slitwidth of 0·2 mm. With the aspirator-nebulizer used in this work, these sensitivity limits can be improved substantially (*ca.* 5-fold) by nebulizing solutions containing solvents to increase the volume of liquid reaching the flame,[11] and possibly also by modulating the radiation from the source to minimize the effects of background radiation and thus permit the use of wider slitwidths (up to 2·0 mm).

Salts of the following selected ions, when present in a 100-fold molar excess over a $10^{-4}M$ bismuth nitrate solution in $4 \times 10^{-2}M$ nitric acid, did not produce a variation of more than 5% in the fluorescence signal; As(III), Cd, Fe(II), Fe(III), K, Na, NH_4, Sb(III) and Zn. Similarly, chloride, nitrate, phosphate, sulphate and tartrate did not interfere. Greater than a 100-fold molar excess of sulphuric acid produced a positive interference because of the strong blue S_2 emission in the diffusion flame.[12] This interference could be eliminated by bleeding a small amount of air into the flame to raise the temperature and oxidize the S_2 species. Aluminium and magnesium in a 100-fold molar excess produced, as expected, significant decreases in the fluorescence signal (40 and 20% respectively).

This interference may be attributed to the formation of oxide particles which "cage" the bismuth and which are not efficiently dissociated by the thermal energy available from the relatively cool diffusion flame. The magnesium suppression may be readily overcome by introducing a small amount of air into the diffusion flame *via* an auxiliary jet in the burner stem.[15] This results in only a slight loss in *overall* sensitivity. In the case of aluminium it was necessary to use an air–hydrogen premixed flame to overcome the interference; the overall sensitivity for bismuth was thereby reduced by *ca.* 50%. Alternatively it may be possible to use an argon–oxygen–hydrogen flame in which the sensitivity loss would not be expected to be so great. There is reason to suppose that many other matrix effects may be readily overcome in the same manner. A diffusion flame burning in oxygen might be equally effective.

Atomic-absorption measurements

Source. The low intensity bismuth electrodeless discharge tubes operated at 40 W with slight cooling were perfectly satisfactory. With the iodine discharge tube as source, a detection limit of 10 ppm was obtained at 2062 Å. This is comparable to the 5·5 ppm detection limit obtained by Manning, Volmer and Fernandez[16] when using a shielded bismuth hollow cathode lamp at the same wavelength.

Flame. The nitrogen–hydrogen and argon–hydrogen diffusion flames used in the fluorescence measurements gave higher (by *ca.* 30%) absorption figures for a given concentration of bismuth than the air–propane and air–acetylene premixed flames when burning on the 7-cm long burner supplied with the instrument. Since background radiation is relatively unimportant in atomic-absorption measurements because the source is modulated (the Unicam SP 900A is operated in its "absorption" mode), the air–propane and air–acetylene flames are recommended to minimize matrix effects. The optimum position for the burner-head was with its top level with the bottom of the monochromator slit.

Table III shows the absorbance measurements obtained at the five resonance lines for a 100-ppm solution of bismuth nebulized into an air–propane flame. The non-resonance line at 3025 Å is included only because of its use in atomic-fluorescence measurements.

The strongest absorption was produced at 2231 Å. At the narrow slitwidths used, this line was completely resolved from the 2228 Å line. It is relevant to note that on this occasion the strongest absorption was not obtained at the same wavelength as the strongest fluorescence signal. The detection limit for bismuth in the present study of atomic-absorbance was found to be 1 ppm and the analytical range 10–100 ppm.

Preparation of calibration curve for atomic-fluorescence

Bismuth solution, 1000-ppm. Dissolve 1·00 g of bismuth metal in 20 ml of concentrated nitric acid and dilute to 1 l. Dilute this solution as required.

Apparatus. The Unicam SP 900A flame spectrophotometer, coupled to a 10-mV Servoscribe recorder, was operated in its "emission" mode. The normal EMI 9529B photomultiplier was replaced by a more ultraviolet-sensitive EMI 9601B photomultiplier.

A "Microtron 200" microwave generator (2450 ± 25 Mc/s) and a model 214L resonant cavity (Electromedical Supplies Limited) were used. Initiation of the discharge was obtained with a simple high-frequency 'Tesla' vacuum-tester.

Flame conditions. A nitrogen–hydrogen diffusion flame was obtained with an acetylene jet in the standard burner base, and the 1·8 × 7·5 cm air–acetylene emission head supplied with the SP 900A (this head is perforated at one end with 13 holes in a 1-cm square). The nitrogen pressure was set at 15 psi and the hydrogen pressure corresponded to 8 cm on the di-n-butyl phthalate manometer gauge. The top of the burner-head was set 3 cm below the bottom of the monochromator slit.

Source conditions. An iodine microwave discharge tube, prepared as described previously, was operated at a power rating of 12 W with a 0·5 cm of the tube extending above and *ca.* 4 cm below the cavity. A moderate degree of cooling was applied by blowing compressed air on the lower 1 cm of tube (the cooling apertures on the cavity were not used). The source was placed *ca.* 8 cm from the centre of the burner-head at right angles to the line from flame to monochromator slit. A 5-mm slit was cut in the burner housing to allow irradiation of the flame.

Procedure. Transfer by pipette 1–10 ml of a 100-ppm bismuth solution into a series of volumetric flasks and dilute to volume with distilled water. Mix and nebulize into the nitrogen–hydrogen flame; use a slitwidth of 0·1 mm, gain 3·1, bandwidth 3, and measure the fluorescence signal at 3025 Å.

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Zusammenfassung—Das Atomfluoreszenzverhalten von Wismutatomen in kalten Stickstoff-Wasserstoff- und Argon-Wasserstoff-Diffusionsflammen, die in Luft brennen, wird beschrieben. Angeregt wird mit der Jodlinie (keine Resonanzlinie) bei 2061,63 Å, die von einer elektrodenlosen, mit Mikrowellen erregten Entladungsröhre emittiert wird, die bei 2450 MHz arbeitet. Man beobachtet die Fluoreszenz der Wismut-Resonanzlinie bei 2061,70 Å sowie direkte Fluoreszenz bei 2697 und 3025 Å. Dazuhin wurden dreizehn andere, viel schwächere Linien beobachtet, sowie zwei nicht identifizierte Linien bei 2880 und 2680 Å. Die Emissionen bei 2628 und 2938 Å rühren offenbar von "thermisch unterstützter direkter Fluoreszenz." Die intensivste Linie bei 3025 Å erlaubt analytische Atomfluoreszenzmessungen mit linearer Anzeige im Bereich 0,1–200 ppm mit einer Nachweisgrenze von 0,05 ppm und keinen Problemen durch Streuung von der Lichtquelle. Hundertfache Konzentrationen von 14 Ionen störten nicht. Matrixeffekte von Aluminium und Magnesium wurden durch Erhöhung der Temperatur der kalten Diffusionsflammen überwunden.

Eine mikrowellenerregte elektrodenlose Wismut-Entladungsröhre wurde als Lichtquelle zur Atomabsorptionsmessung in Luft-Wasserstoff- und Luft-Propan-Flammen bei 2231 Å mit einer Nachweisgrenze von 1 ppm und einem linearen analytischen Bereich von 10–100 ppm verwendet. Mit der Jod-Entladungsröhre war die Nachweisgrenze bei Atomabsorption 10 ppm bei 2062 Å.

Résumé—On décrit les caractéristiques de fluorescence atomique des atomes de bismuth dans les flammes de diffusion froides azote-hydrogène et argon-hydrogène brûlant dans l'air. L'excitation est obtenue par la raie de non résonance de l'iode à 2061,63 Å émise par un tube à décharge sans électrode excité par microndes, opérant à 2450 Mc/s On observe la fluorescence de la raie de résonance du bismuth à 2061,70 Å ainsi que la raie directe de fluorescence à 2697 et 3025 Å. En outre, on a observé treize autres raies beaucoup plus faibles et deux raies non identifiées à 2880 et 2680 Å. Les émissions à 2628 et 2938 Å paraissent provenir de la "fluorescence de raie directe thermiquement assistée". La raie la plus intense à 3025 Å permet des mesures analytiques de fluorescence atomique à fonction linéaire dans le domaine 0,1–200 p.p.m. avec une limite de détection de 0.05 p.p.m. et sans problèmes de diffusion de source.

On n'a pas observé d'interférences pour des concentrations cent fois supérieures de quatorze ions. Les effets de matrice de l'aluminium et du magnésium ont été surmontés en élevant la température des flammes de diffusion froides.

On a utilisé un tube à décharge au bismuth sans électrode excité par micro-ondes comme source pour la mesure d'absorption atomique dans des flammes air-hydrogène et air-propane à 2231 Å avec une limite de détection de 1 p.p.m. et un domaine analytique de relation linéaire de 10–100 p.p.m. Avec le tube à décharge à iode sans électrode excité par micro-ondes, la limite de détection pour l'absorpton atomique a été de 10 p.p.m. à 2062 Å.

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ELECTRON SPIN RESONANCE ANALYSIS OF THE REDOX INDICATOR VARIAMINE BLUE II

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Summary—The oxidation of the redox indicator Variamine Blue in an aqueous medium has been studied by the ESR method. The optimum conditions for the formation of the radical have been determined. The spectra have in some cases shown hyperfine splitting, from which conclusions could be drawn for the nature of the oxidation reaction and structure of the oxidized product. The coupling constants have also been determined for the radicals. The correctness of the assumptions for the structure of the radicals has been supported by the simulation of spectra and the investigation of deuterated derivatives.

VARIAMINE Blue [*N*-(*p*-methoxyphenyl)phenylenediamine] is a redox indicator used in analytical chemistry.[1] Its oxidation mechanism has been investigated by different methods.[2] The potentiometric titration curves obtained for Variamine Blue have shown that relatively stable intermediates are formed during its oxidation. The paramagnetic properties of the intermediates have earlier been proved[3] by ESR analysis. These measurements have been carried out partly on the solid oxidation product isolated from benzene and partly on the aqueous suspension of the product. Owing to the experimental techniques used, no hyperfine splitting could be observed. Therefore the structure of the radical or radical ion could not be studied in detail.

In the present experiments water was used as solvent, both the original compound and its oxidation products being soluble in it; moreover, water is used as the solvent in practice when Variamine Blue is used as an indicator. The high dielectric constant of water, however, is disadvantageous in an ESR investigation, and makes necessary the tedious removal of oxygen by freezing out. The application of capillary cuvettes, however, enabled us to produce spectra which gave information on the structure of radicals formed during the oxidation of Variamine Blue.

EXPERIMENTAL

Variamine Blue and its derivatives used for the investigations were prepared in our laboratories. The compounds were of analytical purity. ESR measurements were carried out with a JES-P-10 type ESR spectrometer. The oxidation products were separated by thin-layer chromatography.

The influence of the pH of the solution, of the stoichiometry of the oxidation reaction, of the nature of the oxidizing agent and of the concentration of the dyestuff have been studied. The change of radical ion concentration has also been measured as a function of time. All measurements were made at room temperature.

The concentration of the radical ion was supposed to be proportional to the height of the amplitude of the derivative curve. The simulated spectra were constructed on a JRA-1 "Spectrum Accumulator".

RESULTS AND DISCUSSION

pH-Dependence of the radical ion concentration

According to earlier measurements the indicator can be used in the pH range between 2 and 6.[4] The formation and concentration of the radical ion have therefore been investigated in our present experiments in the pH range between 0·5 and 5. The compound was oxidized with the Ag^+/Ag redox system, one mole of Variamine Blue being allowed to react with one mole of silver nitrate. The pH was checked in each determination. Figure 1 shows the pH-dependence of the relative radical

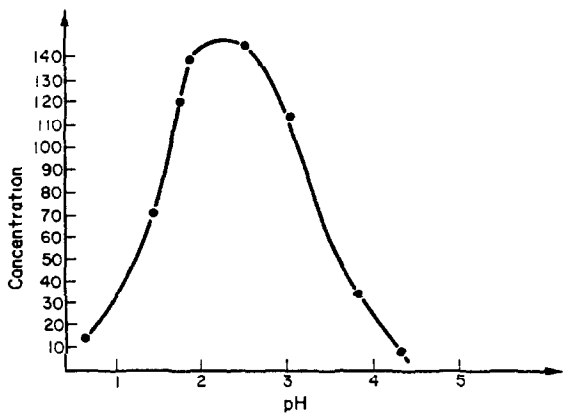


FIG. 1.—pH-Dependence of relative radical concentration.

concentration. The maximum radical ion concentration occurs between pH 2 and 3. As shown by Fig. 1, at pH 1 and pH $>$ 4 hardly any radical ion is present in the solution. Hence the indicator can be used in a wider pH range than that in which the radical ion can exist, and it seems likely that the colour of the oxidized form cannot be attributed to the radical ion.

Influence of the stoichiometry of the oxidation reaction on the radical ion concentration

When three different oxidizing agents were used in buffered solutions, in each case the maximum values of the radical ion concentration occurred at about $\tau = 1$ (Fig. 2). However, the presence of radical ions in small amounts, even at degree of oxidation corresponding to the transfer of two electrons, indicates that the oxidation reaction of the compound is more involved than that assumed to result in the quinone di-imine oxidized form *via* a semiquinone intermediate. It seems likely that the oxidation involves several reaction sequences proceeding in parallel. This assumption has been proved by thin-layer chromatographic separations.

Effect of the nature of the oxidizing agents

The normal redox potential has no influence on the character of the spectrum, but only on the concentration of the radical ion (Fig. 2). The Ce(IV)/Ce(III), Ag^+/Ag and Br_2/Br^- systems were investigated. According to the results of chromatographic separations, products obtained at different dyestuff to oxidant ratios are the same for both the Ag^+/Ag and Ce(IV)/Ce(III) systems, but some of the products obtained with an excess of oxidant are different.

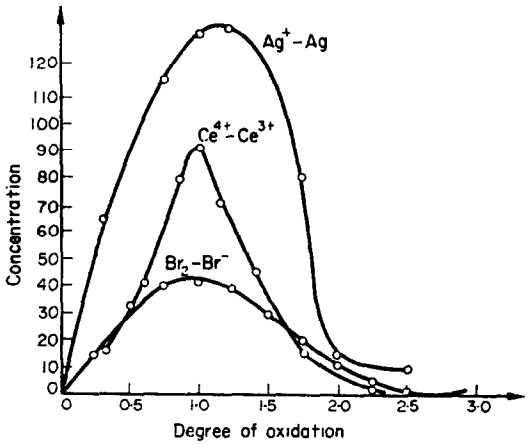


FIG. 2.—Dependence of relative radical concentration on the degree of oxidation.

The change of radical ion concentration with time

The initial period of decomposition has been found to be kinetically second-order (Fig. 3). The shapes of the curves obtained for oxidation with different oxidizing agents have been found to be the same. The reduction of radical ion concentration can be due to recombination or disproportionation. On the basis of experience

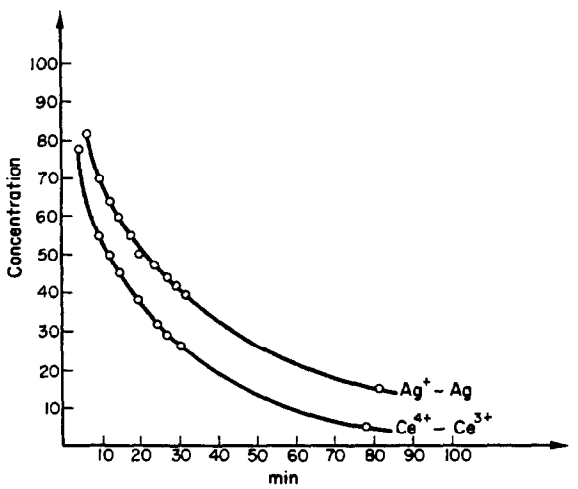


FIG. 3.—Dependence of relative radical concentration on time.

gained in earlier experiments, all concentration determinations were started at a fixed time after mixing the reagents. The amount of radical ion produced is proportional to the initial concentration of reagents. The relationship has been investigated in the concentration range between about 4×10^{-3} and $4 \times 10^{-2} M$; the limits are determined by the signal-to-noise ratio of the instrument and by the solubility of the compound.

Measurement of radical ion concentration

The ratio of radical ion concentration to the produced and initial Variamine Blue concentration has also been studied. Frémy's salt was used as standard. It has been

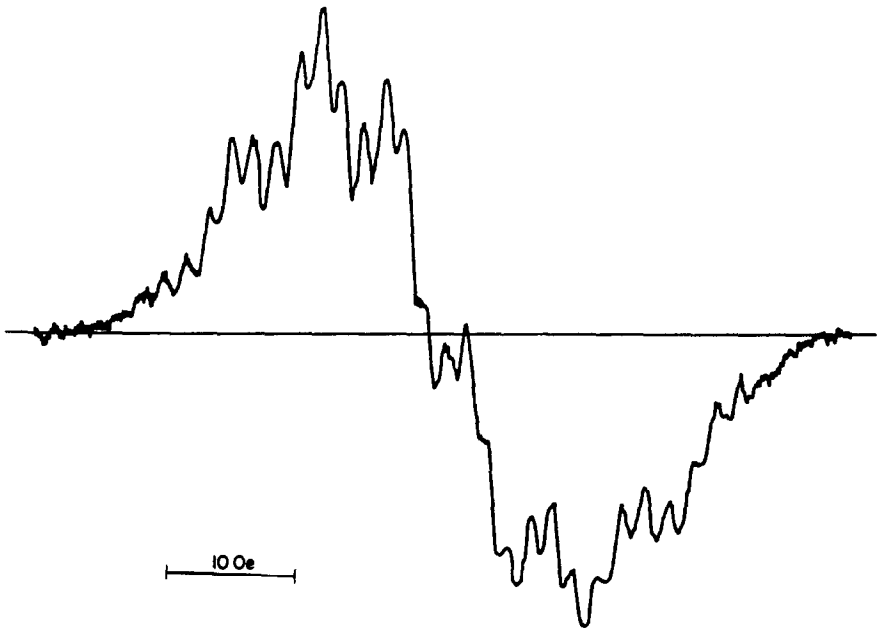


FIG. 4.—ESR spectrum of the radical ion of Variamine Blue.

found by comparing double integrals of the ESR signals that, even under optimal experimental conditions, the paramagnetic intermediate is only formed from 3% of the initial compound in aqueous medium.

Interpretation of the hyperfine splitting of the spectra

The ESR spectrum of oxidized Variamine Blue taken under oxygen-free conditions is shown in Fig. 4. The line diagram in Fig. 5a was drawn by a JRA-1 Spectrum Accumulator. The spectrum contains 8–9 groups of lines which are not well resolved, and 29 lines altogether. No spectrum with better separation could be obtained. In

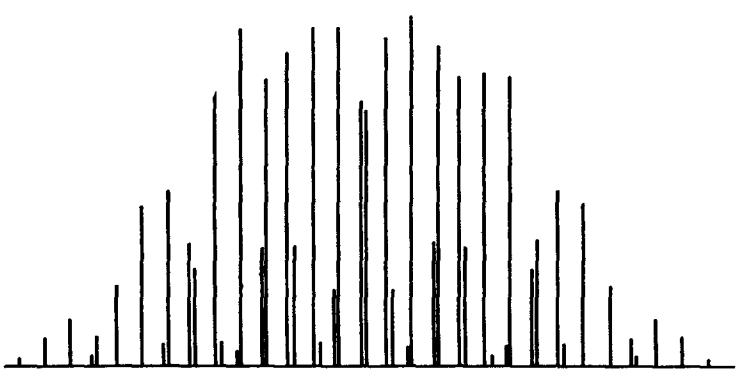
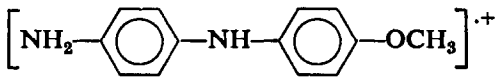


FIG. 5a.—Line diagram of the ESR spectrum of Variamine Blue.

the interpretation of the spectra, literature data concerning the structure of Wurster-type radicals were used.

It has been assumed that the hyperfine splitting of the spectrum is due to the interactions between the two equivalent nitrogen atoms, the three hydrogen atoms attached to them, four further hydrogen atoms and an unshared electron. The radical ion can be assumed to be



The two nitrogen atoms are equivalent because, to a first approximation, the electrophile property of the phenyl group B can be considered as equivalent to the electron repelling effect of the methoxy group in the *para* position, and therefore no large electron shift is caused on the secondary nitrogen atom by the *p*-anisyl group. It also follows that the three hydrogen atoms attached to the two nitrogen atoms are also equivalent. The ratio of the coupling constants of nitrogen and hydrogen atoms can be taken as 3:4 on the basis of the spectra and also from literature data.[5,6,7] The coupling constant for the ring and the four equivalent hydrogen atoms attached to it has been found to be 1. On the basis of these considerations calculations have been made for the simulation of the experimental spectrum. According to these the best coincidence has been obtained with the following coupling constants: $a_N = 5{\cdot}6$ Oe (2N), $a_H = 7{\cdot}6$ Oe (3H), $a_H = 2{\cdot}0$ Oe (4H), and the line width measured between the maxima of the derivative curve was $\Delta H_m = 2{\cdot}3$ Oe. The Lorentz line-shape has been used in the simulation, and no attempt has been made to determine line width correctly. A line diagram and the spectrum calculated by means of the data above are shown in Figs. 5a and 5b respectively. The formation of a radical of the proposed

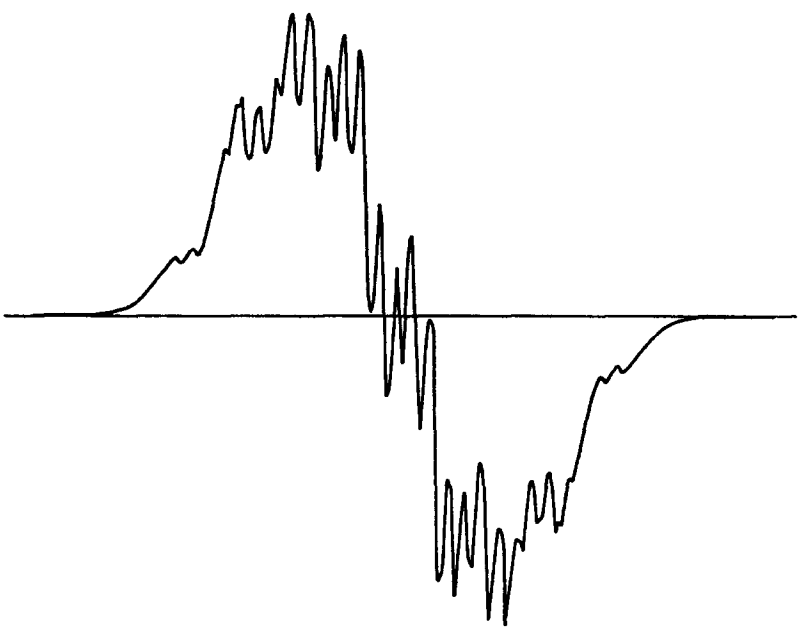


FIG. 5b.—Simulated ESR spectrum of the radical ion of Variamine Blue.

structure is in agreement with our earlier investigations and can be described as follows:

$$\text{Red} \overset{-H^+ \; -e}{\rightleftharpoons} \text{Sem} \rightleftharpoons \tfrac{1}{2}\,\text{Dim} \overset{-H^+ \; -e}{\rightleftharpoons} \text{Ox}$$

or

$$\text{Ox} + \text{Red} \rightleftharpoons 2\,\text{Sem} \rightleftharpoons \text{Dim}$$

where Sem = Semiquinone and Dim = dimer.

The existence of the reactions leading to equilibrium was established by thin-layer chromatographic measurements. If the amount of oxidizing agent corresponding to the transfer of one electron was added to the reduced form, and the mixture separated

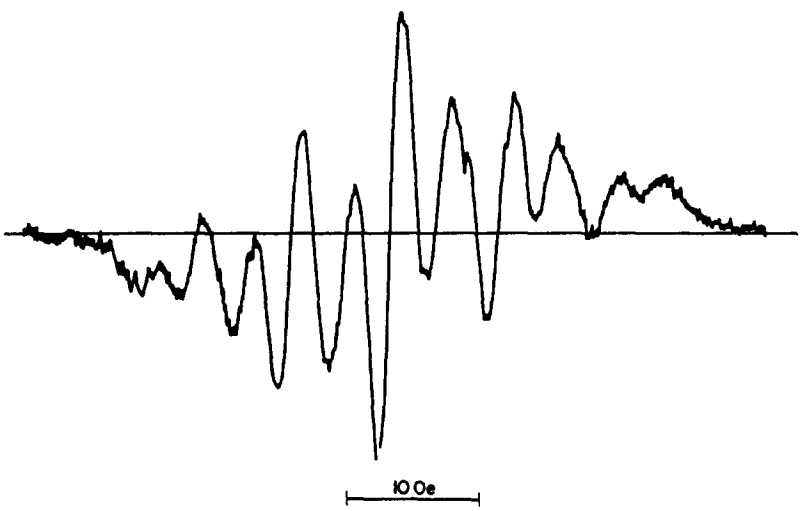


FIG. 6.—ESR spectrum of the *N*-acetyl derivative of Variamine Blue.

by thin-layer chromatography, the initial compound and the oxidized product corresponding to the transfer of two electrons could be found as well as the intermediate. Some unidentified polymeric material was also found. There was also evidence of the production of compounds from a further reaction of *p*-quinonedi-imine. As shown by the relatively small amount of radical ion, the equilibrium between semiquinone and dimer is shifted towards the formation of dimer.

Some derivatives (2-CH_3, 2-CH_3O, 2-COOH, 2-SO_3H and 2-SO_2NHPh) of Variamine Blue have also been studied. All produce an ESR signal, but the splitting in the spectra is not satisfactory. The ESR spectrum of the *N*-acetyl derivative gives good splitting, in which 11 relatively broad lines have been observed (see Fig. 6).

In spite of the fact that the spectrum shows relatively good splitting, two interpretations are possible. The spectrum is essentially a quintet, all the lines of which can be split (*a*) to a triplet with intensity ratios 1:2:1, or (*b*) to a quintet with intensity ratios 1:4:6:4:1. Since the lines partly coincide, only 11 lines can be observed, the widths of neighbouring lines being different because of the inaccuracy of coincidence.

The spectrum corresponding to assumption (b) should contain 13 lines, the two smallest of which (at the ends) overlap with their neighbours almost entirely. The spectra can be simulated by using the following parameters.

(*a*) $a_N = 7{\cdot}6$ Oe (2N), $a_H = 3{\cdot}1$ Oe (2H) and $\Delta H_m = 2{\cdot}1$ Oe

(*b*) $a_N = 7{\cdot}6$ Oe (2N), $a_H = 3{\cdot}0$ Oe (4H) and $\Delta H_m = 2{\cdot}1$ Oe

The simulated spectra are shown in Figs. 7a and 7b, respectively. Analogous reactions have been carried out in heavy water with the purpose of exchanging hydrogen atoms attached to the nitrogen atom for deuterium atoms. The spectra of the deuterated

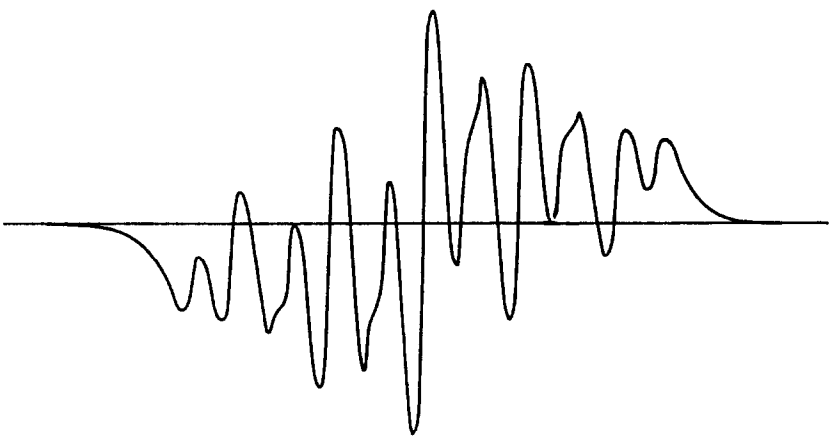


FIG. 7a.—Simulated ESR spectrum of the *N*-acetyl derivative in case (*a*).

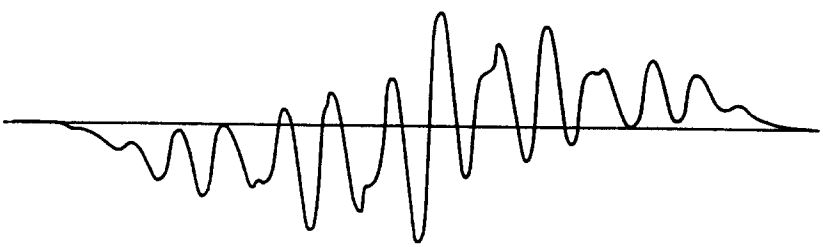


FIG. 7b.—Simulated ESR spectrum of the *N*-acetyl derivative in case (*b*).

products can be interpreted in agreement with the statements above and with the chemical properties of the compounds. The width of the spectrum of deuterated Veriamine Blue was found to be three-quarters that of the original, owing to the difference of the coupling constants for hydrogen and deuterium (Fig. 8). No splitting of the spectrum could be observed.

The simulated spectra show that these changes of the spectrum are to be expected (Figs. 9a and 9b). The $a_{D(N)}$ coupling constant has been calculated from the $a_{H(N)}$ coupling constant, taking the magnetic moments and nuclear spins into consideration

$$\left(a_D/a_H = \frac{\mu_D}{I_D} \cdot \frac{I_H}{\mu_H} = \frac{0{\cdot}8574}{1} \times \frac{1/2}{2{\cdot}7928} = 1/6{\cdot}51\right).$$

Because of this and the actual line-width the lines must coalesce.

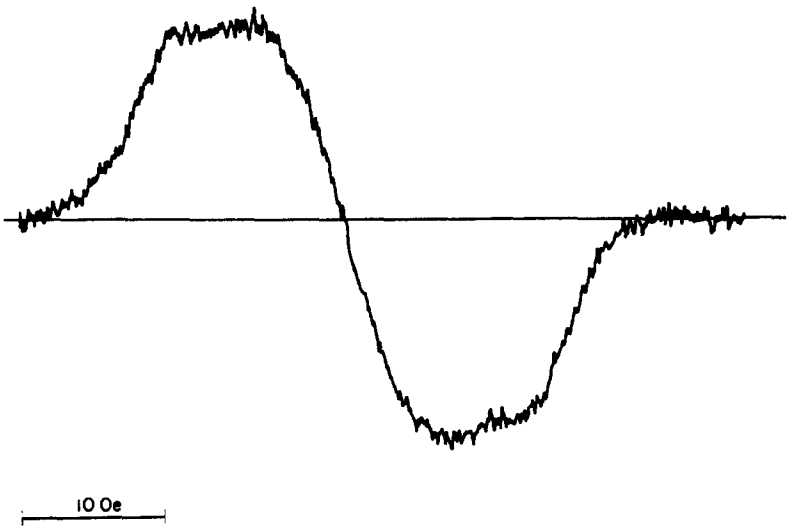


FIG. 8.—ESR spectrum of the radical ion of Variamine Blue in heavy water.

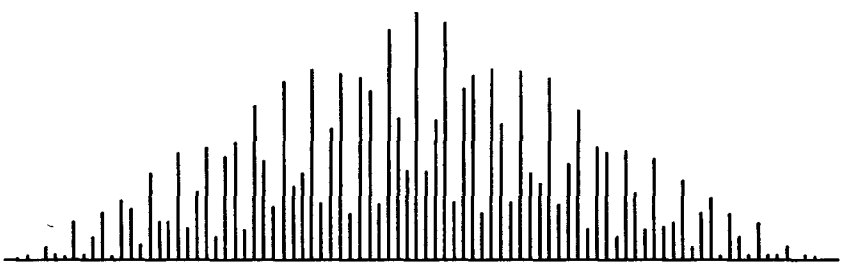
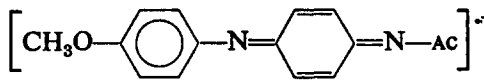


FIG. 9a.—Line diagram of the spectrum shown in Fig. 8.

FIG. 9b.—Simulation of the spectrum shown in Fig. 8.

In contradiction to this, no change could be observed in the spectrum of the *N*-acetyl derivative under the given conditions, indicating that hydrogen–deuterium exchange has not taken place. This could be due to the reduced basicity of the *N*-acetyl derivative. One cannot, however, reasonably assume that this reduction in basicity would be large enough to make the exchange impossible even in strongly acidic solution. Therefore it seems more likely that the radical does not contain hydrogen atoms attached to nitrogen atoms, *i.e.*, its structure can be assumed to be



This structure corresponds to the transfer of three electrons but is in agreement with such facts as the low radical concentration. The ratio of coupling constants (a_H/a_N = 0·40) also suggests that the protons causing splitting are attached to the ring and not to nitrogen atoms (for Variamine Blue $a_{H(N)}/a_N$ = 1·36, and a_H/a_N = 0·36). The spectrum of the *N*-acetyl derivative can be therefore interpreted by assumption (b), and the structure described above.

Acknowledgement—We should like to thank B. Turcsányi and G. Koszterszitz for their help with the measurements and interpretation of spectra.

Zusammenfassung—Die Oxidation des Redoxindikators Variaminblau in wäßriger Lösung wurde mit der Elektronenspinresonanzmethode untersucht. Die optimalen Bedingungen zur Bildung des Radikals wurden ermittelt. Die Spektren zeigten in einigen Fällen Hyperfeinstrukturaufspaltung, aus der Schlüsse über die Natur der Oxidationsreaktion und die Struktur des oxidierten Produkts gezogen werden konnten. Die Kopplungskonstanten der Radikale wurden auch bestimmt. Die Richtigkeit der Annahmen über die Struktur der Radikale wurde bekraftigt durch die Simulierung von Spektren und die Untersuchung deuterierter Derivate.

Résumé—On a étudié l'oxydation de l'indicateur redox Bleu de Variamine en un milieu aqueux par la méthode RSE. On a déterminé les conditions optimales pour la formation du radical. Dans quelques cas, les spectres ont montré un dédoublement hyperfin, à partir duquel on a pu tirer des conclusions sur la nature de la réaction d'oxydation et la structure du produit oxydé. On a également déterminé les constantes de couplage pour les radicaux. L'exactitude des hypothèses pour la structure des radicaux a été étayée par la simulation de spectres et l'étude de dérivés deutérés.

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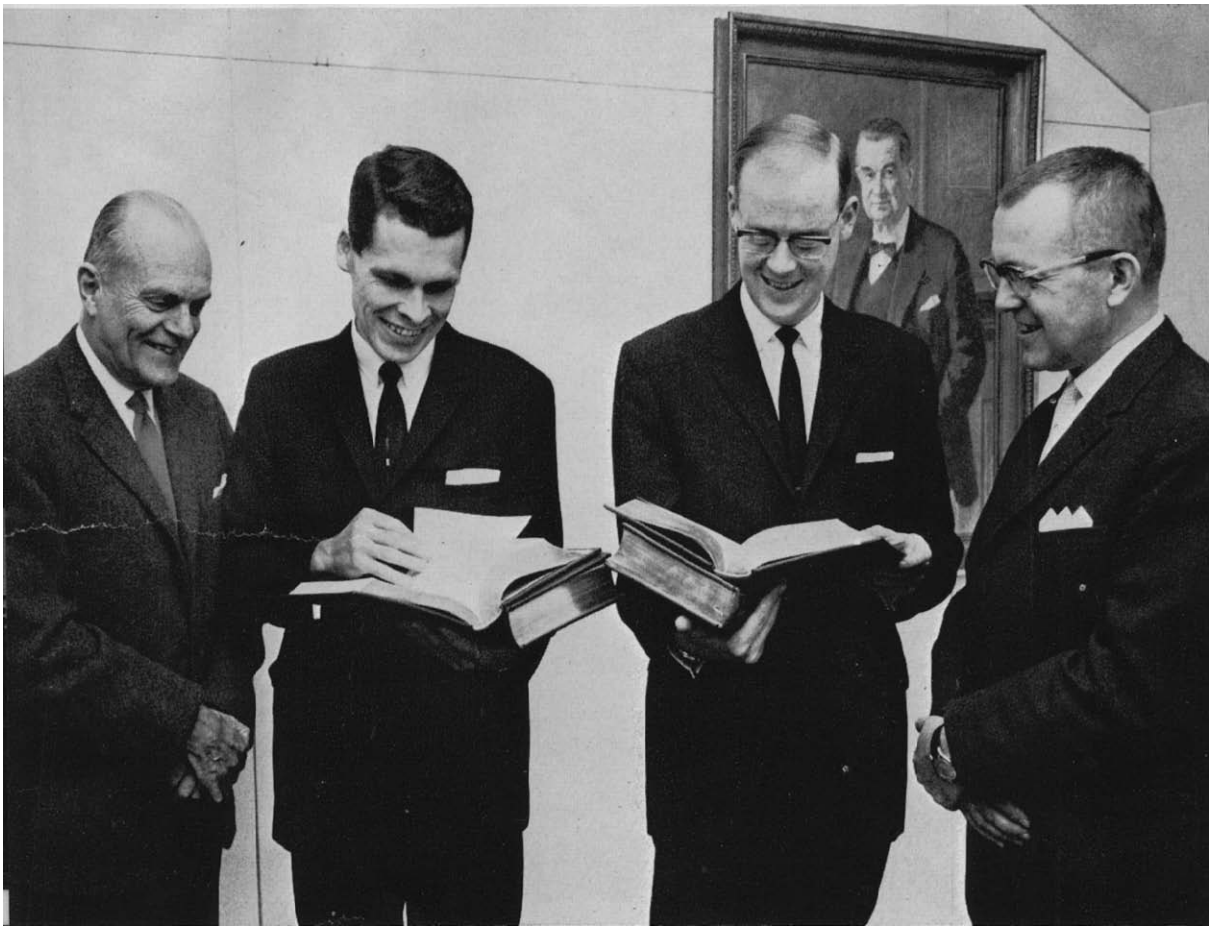

Louis Gordon Memorial Award 1966

EBBE STILL and FOLKE INGMAN inspect the specially bound copies of *Talanta* 1966, which volume contains their paper "Graphic Method for the Determination of Titration End-points", chosen for the Louis Gordon Memorial Award 1966 (see *Talanta*, 1967, **14**, *facing* p. 693). The copies were presented on 6th October in the authors' Institute at Åbo Academy, Finland, by Dr. ERKKI WÄNNINEN (Member of the Advisory Board of *Talanta*) in the presence of Professor ANDERS RINGBOM (*extreme left*). The portrait on the wall is of Professor Emeritus Jarl Salin.

Talanta, 1967, Vol. 14, p. i. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry: Editor, G. SNATZKE Heyden, London, 1967. pp. 416. 96s.

This collection of invited lectures, given at the N.A.T.O. Summer School on Optical Rotatory Dispersion and Circular Dichroism, Bonn, 1965, although primarily devoted to applications in organic chemistry, also includes significant contributions on inorganic, biochemical and high polymer topics. The opening chapters, contributed by some of those most responsible for the recent widespread renewal of interest and activity in the subject, form an excellent introduction for those unfamiliar with O.R.D. and C.D. The succeeding chapters well illustrate the tremendous range of modern developments in the field, that on magnetically induced optical activity being particularly valuable. The volume is well produced and the text adequately illustrated with diagrams and formulae. Particularly useful as an introduction both to the phenomena of O.R.D. and C.D. and to current developments this book will appeal to those interested in optical activity at any level.

Reagent Chemicals and Standards, 5th Ed: JOSEPH ROSIN. Van Nostrand, Princeton, New Jersey, 1967. pp. vii + 641. 132s.

The most significant addition to the text in this latest edition is a section dealing with the technique of flame photometry. This has been necessitated by the wide application of this technique in the analysis of trace impurities and many methods based on flame photometry are described separately. Among the other additions are new reagents and dyes such as osmium tetroxide and Eriochromecyanine.

Progress in Nuclear Energy, Series IX, Analytical Chemistry, Vol. 8, Pt. 1: Editors, H. A. ELION and D. C. STEWART, Pergamon, Oxford, 1967. pp. 139. 45s.

This volume contains three well-grouped articles on the analytical chemistry of protactinium (D. Brown and A. G. Maddock) and actinium (H. W. Kirby) and analysis of essential nuclear reactor materials by extraction photometry with oxine and 2-methyloxine. All show evidence of practical experience, sometimes painfully gained, and this is reflected in a lively style. The sections on protactinium and actinium also contain much information of general chemical interest. The standard of production of the series is maintained; though flexi covers have replaced hard covers the price per page remains constant.

Methodes D'Analyse, CETAMA-1966, Methodes 151-200: Commissariat a L'Energie Atomique, Presses Universitaires de France, Paris, 1967. F 75.

This is a collection of tried and proven methods of analysis used in French atomic energy establishments. Each is laid out in an exemplary way, with extremely clear instructions on how to prepare for the analysis, how to execute it and how to treat the results. Although the methods are devised for materials of specialized interest, many would appear to have general applicability. Many approaches are used, *e.g.*, titrimetry, spectrophotometry, fluorimetry, neutron-activation, spectrography, polarography and radioactivity, and methods for thirty different elements are reported.

ERRATUM

D. A. BEARDSLEY, G. B. BRISCOE, J. RŮŽIČKA and M. WILLIAMS: Substoichiometric determination of traces of gold by radioactive isotope-dilution analysis, *Talanta*, 1967, **14**, 879–886.

Page 883, Table IV: Under "Foreign ion interfering", in the 1000-μg column "Bi(III)†" should read "Bi(III)††", and in the 100-μg column "Cu(II)‡" should read "Cu(II)††".

Talanta, 1967, Vol. 14, p. i. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry: Editor, G. SNATZKE Heyden, London, 1967. pp. 416. 96s.

This collection of invited lectures, given at the N.A.T.O. Summer School on Optical Rotatory Dispersion and Circular Dichroism, Bonn, 1965, although primarily devoted to applications in organic chemistry, also includes significant contributions on inorganic, biochemical and high polymer topics. The opening chapters, contributed by some of those most responsible for the recent widespread renewal of interest and activity in the subject, form an excellent introduction for those unfamiliar with O.R.D. and C.D. The succeeding chapters well illustrate the tremendous range of modern developments in the field, that on magnetically induced optical activity being particularly valuable. The volume is well produced and the text adequately illustrated with diagrams and formulae. Particularly useful as an introduction both to the phenomena of O.R.D. and C.D. and to current developments this book will appeal to those interested in optical activity at any level.

Reagent Chemicals and Standards, 5th Ed: JOSEPH ROSIN. Van Nostrand, Princeton, New Jersey, 1967. pp. vii + 641. 132s.

The most significant addition to the text in this latest edition is a section dealing with the technique of flame photometry. This has been necessitated by the wide application of this technique in the analysis of trace impurities and many methods based on flame photometry are described separately. Among the other additions are new reagents and dyes such as osmium tetroxide and Eriochromecyanine.

Progress in Nuclear Energy, Series IX, Analytical Chemistry, Vol. 8, Pt. 1: Editors, H. A. ELION and D. C. STEWART, Pergamon, Oxford, 1967. pp. 139. 45s.

This volume contains three well-grouped articles on the analytical chemistry of protactinium (D. Brown and A. G. Maddock) and actinium (H. W. Kirby) and analysis of essential nuclear reactor materials by extraction photometry with oxine and 2-methyloxine. All show evidence of practical experience, sometimes painfully gained, and this is reflected in a lively style. The sections on protactinium and actinium also contain much information of general chemical interest. The standard of production of the series is maintained; though flexi covers have replaced hard covers the price per page remains constant.

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ERRATUM

D. A. BEARDSLEY, G. B. BRISCOE, J. RŮŽIČKA and M. WILLIAMS: Substoichiometric determination of traces of gold by radioactive isotope-dilution analysis, *Talanta*, 1967, **14**, 879–886.

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Talanta, 1967, Vol. 14, p. i. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Quantitative Papierchromatographie inaktiver Substanzen durch radioaktive Zusätze—I: GERHARD ACKERMANN and EGON WEBER (8 *May* 1967)

Gravimetric determination of caesium and potassium with sodium triphenylcyanoborate: A. BAUMAN (21 *July* 1967)

Spectrophotometric determination of germanium(IV) with Pyrogallol Red: G. POPA and I. PARALESCU (21 *July* 1967)

Catalytic microdetermination of chromium: T. P. HADJIIOANNOU (24 *July* 1967)

Precipitation of bis(1,2-cyclohexanedionedioxinato)palladium(II) from homogeneous solution: J. A. VELÁZQUEZ and O. E. HILEMAN, JR. (27 *July* 1967)

Absorption of ions of the first row transition metals on to the chelating resin Dowex A-1: D. G. BIRNEY, W. E. BLAKE, P. U. MELDRUM and M. E. PEACH (31 *July* 1967)

Amperometric titrations of alkali thiomolybdate with lead(II): R. S. SAXENA and M. C. JAIN (31 *July* 1967),

Bemerkungen zum Verfahren der Gegenstromionophorese: W. PREETZ (31 *July* 1967)

Extraction of certain elements from water–methanol, ethanol and acetone mixtures by tridodecylamine and tributyl phosphate: A. ALIAN, H. KHALIFA and W. SANAD (1 *August* 1967)

Substituents of esters of the phosphonic acids, as reagents for the separation of molybdenum from rhenium by extraction: N. JORDANOV, ST. MAREVA, G. BORISOV and B. JORDANOV (4 *August* 1967)

Spectrophotometric study of the reaction of tervalent iron with Methylthymol Blue: BORISLAV KARADAKOV, DONKA KANTCHEVA and PETRANA NENOVA (4 *August* 1967)

Anion-exchange behaviour of the platinum metals and gold in hydrochloric acid–organic solvent media: J. KORKISCH and H. KLAKL (7 *August* 1967)

Prüfung der flammenphotometrischen Anionenstörung I. Untersuchung der Aluminiumstörung: E. PUNGOR and Á. SZÁSZ (7 *August* 1967)

Substoichiometric determination of molybdenum in steels by neutron-activation analysis: R. A. NADKARNI and B. C. HALDAR (8 *August* 1967)

Homogeneous nucleation of calcium hydroxide: D. H. KLEIN and N. D. SMITH (8 *August* 1967)

Note on the iodimetric estimation of arsenious sulphide: P. B. JANARDHAN and AGNES PAUL (9 *August* 1967)

Note on the arsenic species in alkaline solutions: P. B. JANARDHAN and AGNES PAUL (9 *August* 1967)

The system aluminium(III)–dipicolinic acid in aqueous 0.5M sodium perchlorate medium: ALDO NAPOLI (10 *August* 1967)

Studies in atomic-fluorescence spectroscopy—VII. The fluorescence and analytical characteristics of arsenic, using a microwave excited electrodeless discharge tube as source: R. M. DAGNALL, K. C. THOMPSON and T. S. WEST (10 *August* 1967)

Adsorption of cations from formic acid solutions on Dowex 50W-XS. Separation of zirconium(IV) and thorium(IV). MOHAIN QURESHI, WAQIF HUSAIN and A. H. ISRAILI (14 *August* 1967)

Rapid determination of copper in plants by neutron-activation analysis: APOSTOLOS P. GRIMANIS (14 *August* 1967)

Compleximetric titration of water hardness by a simple visual procedure: B. FLEET, SOE-WIN and T. S. WEST (15 *August* 1967)

Compleximetric titration of calcium in the presence of a large amount of magnesium: S. TSUNOGAI, M. NISHIMURA and S. NAKAYA (15 *August* 1967)

Characteristic metal-halogen frequencies of complexes with bivalent metal halides: R. H. NUTTALL (16 *August* 1967)

Talanta, 1967, Vol. 14, p. i. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Rapid ultra-trace determination of beryllium by gas chromatography: WILLIAM D. ROSS and ROBERT E. SIEVERS (22 *May* 1967)

Activation analysis: Determination of sodium in high purity silica: B. T. KENNA and F. J. CONRAD (13 *June* 1967)

Estimation of minimum detectable sample concentrations obtained with near and middle infrared detectors for infrared absorption spectrophotometry: J. D. WINEFORDNER, J. J. CETORELLI and W. J. MCCARTHY (19 *June* 1967)

Use of submicroanalysis and flame ionization detecting gas–liquid chromatograph in the identification of electrolysis products at the dropping mercury electrode: D. BARNES, R. BELCHER and P. ZUMAN (21 *June* 1967)

Preliminary investigation of the application of electroluminescence techniques to the determination of aromatic hydrocarbons: B. FLEET, G. F. KIRKBRIGHT and C. J. PICKFORD (22 *June* 1967)

Spectroscopy in separated flames—II. The use of the separated air–acetylene flame in atomic absorption spectroscopy: D. N. HINGLE, G. F. KIRKBRIGHT and T. S. WEST (22 *June* 1967)

Studies in imidazole derivatives as chelating agents—IV. Stability constants of the metal chelates of azomidazoles: OSAMU YAMAUCHI, HISASHI TANAKA and TOYOZO UNO (22 *June* 1967)

Studies on imidazole derivatives as chelating agents—V. Investigations of the applicabilities of the azomidazoles as metallochromic indicators: OSAMU YAMAUCHI, HISASHI TANAKA and TOYOZO UNO (22 *June* 1967)

Determination of potassium in fertilizers and related materials by an automatic UV absorption method: J. M. SKINNER and A. C. DOCHERTY (26 *June* 1967)

Comparisons of metal bath techniques in vacuum fusion analysis by an isotope dilution method: H. KAMADA and K. FURUYA (27 *June* 1967)

Spectrophotometric study of the mercury(II)–Xylenol Orange chelate: H. H. WALKER and J. A. POOLE (28 *June* 1967)

Cation-exchange behaviour of several elements in hydrofluoric acid-organic solvent media: J. KORKISCH and A. HUBER (3 *July* 1967)

Gravimetric determination of perchlorate ion as tetraphenylarsonium perchlorate: TEIJI OKUBO and FUMIO AOKI (3 *July* 1967)

Spectrophotometric determination of ferric ions with *o*-hydroxybutyrophenone oxime: M. H. GANDHI and MAHENDRA N. DESAI (3 *July* 1967)

Spectrophotometric determination of iron with 2,4-dihydroxybutyrophenone oxime: M. H. GANDHI and MAHENDRA N. DESAI (3 *July* 1967)

Flavones as analytical reagents—A review: MOHAN KATYAL (4 *July* 1967)

Spectrophotometric study and micro-determination of copper by the pyridine-phenylpyruvic acid oxime system: MOHAN KATYAL, K. C. TRIKHA and R. P. SINGH (4 *July* 1967)

Precipitation of beryllium in presence of succinate by the urea hydrolysis technique: T. P. PRASAD and M. N. SASTRI (4 *July* 1967)

Extraction of titanium(IV) gallate into tri-isoctylamine and its spectrophotometric determination: KULUMANI R. KRISHNAMURTHY and CH. VENKATESWARLU (5 *July* 1967)

Use of 1-phenyl-3-methyl-4-capryl-pyrazolone-5 in the liquid-liquid extraction method for the carrier free production of ^{115m}In: M. Y. MIRZA (10 *July* 1967)

Volumetric determination of the U/O-ratio in uranium oxides: J. J. ENGLEMAN, J. KNAAPE and J. VISSER (10 *July* 1967)

Determination of palladium, platinum and rhodium in geologic materials by fire assay and emission spectrography: JOSEPH HAFFTY and LEONARD B. RILEY (14 *July* 1967)

Kinetic titration with thermometric determination of the end-point: I. SAJÓ (14 *July* 1967)

Spectrophotometric determination of aluminium with Eriochrome Azurol B: HIRAKO KANEKO and KEIJI KANEKO (18 *July* 1967)

Metal chelates of uranium(VI) and thorium(IV) with ammonium aurintricarboxylate: a potentiometric study: AMITAV BANERJEE and ARUN. K. DEY (18 *July* 1967)

Metal chelate exchange in the organic phase—II. Extraction and exchange constants of dithizonates and diethyldithiocarbamates: J. STARÝ and J. RŮŽIĆKA (18 *July* 1967)

Talanta, 1967, Vol. 14, p. i. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Elektronisches Rechnen in den Analytischen Chemie—IV. Algol-Prozedur für Ausgleichsfunktionen mit zwei Konstanten: G. GOTTSCHALK (26 *April* 1967)

Gravimetric and spectrophotometric determination of hexafluoroantimonate utilizing tetraphenylarsonium chloride, nitron and ferroin: VERNON S. ARCHER and RONALD B. TWELVES (19 *May* 1967)

Continuous substoichiometric determination of traces of mercury by radioactive isotope-dilution analysis: G. B. BRISCOE, B. G. COOKSEY, J. RŮŽIČKA and M. WILLIAMS (22 *May* 1967)

Determination of tervalent chromium and iron in chromic acid: D.L. FUHRMAN and G. W. LATIMER, JR. (22 *May* 1967)

Controlled potential coulometric determination of uranium and neptunium in uranium-neptunium alloys: C. E. PLOCK and W. S. POLKINGHORNE (25 *May* 1967)

Studies of current-time curves of mature polarized mercury drops: S. LAL, P. S. JAIN and S. N. SRIVASTAVA (26 *May* 1967)

Analytical applications of ternary complexes—V. Indirect spectrophotometric determination of cyanide: R. M. DAGNALL, M. T. EL-GHARMY and T. S. WEST (29 *May* 1967)

Spektrophotometrische Bestimmung von Kupfer mit 2.3.8.9-dibenzo-4,7-dimethyl-5.6-dihydro-1.10-phenanthrolin (Cuprotest): G. ACKERMANN and W. ANGERMANN (29 *May* 1967)

Neutron-activation analysis by standard addition and solvent extraction. Determination of traces of antimony: A. ALIAN, B. ALIAN and H. KHALIFA (31 *May* 1967)

Polarographic currents in potassium peroxydisulphate—alkali systems and the analysis of peroxydisulphate ion: E. HAKOILA (5 *June* 1967)

Remarks on hexaminecobalt(III)carbonatoberyllate: R. G. MONK (5 *June* 1967)

Investigation of magnesium ammonium phosphate by derivatography: F. PAULIK, E. BUZÁGH-GERE and L. ERDEY (5 *June* 1967)

Replacement substoichiometry and its application in activation analysis: IVAN OBRUSNÍK and ARNOLD ADÁMEK (6 *June* 1967)

Switching valves for use in multi-column gas chromatography: J. R. CONDER, J. H. PURNELL and R. WALSH (12 *June* 1967)

Identification of thiols by means of mercurated fluorescein: MIECZYSLAW WRONSKI (13 *June* 1967)

Note on the various methods of ion separation by electrolytic migration in a counter-current solution: D. BEHNE, B. A. BILAL, H. D. FREYER and W. THIEMANN (14 *June* 1967)

Studies in atomic-fluorescence spectroscopy—VI. The fluorescence characteristics and analytical determination of bismuth, using an iodine electrodeless discharge tube as source: R. M. DAGNALL, K. C. THOMPSON and T. S. WEST (14 *June* 1967)

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PAPERS RECEIVED

Mass spectrometry of metal chelates—II. Oxinates of common metals: A. E. JENKINS, J. R. MAJER and M. J. READE (24 *April* 1967)

Neutron-activation analysis of manganese in polysulphide materials: F. J. CONRAD and B. T. KENNA (24 *April* 1967)

Determination of organic fluoride down to 0·2 ppm in hydrocarbons: M. MILLER and D. A. KEYWORTH (26 *April* 1967)

Determination of stable strontium environmental media: A. B. STRONG, G. L. REHNBERG and U. R. MOSS (27 *April* 1967)

High-speed computers as a supplement to graphical methods. HALTAFALL, a general program for calculating the composition of equilibrium mixtures: NILS INGRI, WŁAYYSŁAW KAKOŁOWICZ, LARS GUNNAR SILLÉN and BJÖRN WARNQVIST (27 *April* 1967)

A novel multi-column gas chromatograph system: J. H. PURNELL and B. C. SHURLOCK (27 *April* 1967)

Determination of microamounts of beryllium in urine: S. R. DESAI and KUM. K. SUDHALATHA (1 *May* 1967)

Microdetermination of the azide group in organic compounds: W. I. AWAD, Y. A. GAWARGIOUS and S. S. M. HASSAN (2 *May* 1967)

Electron spin resonance analysis of the redox indicator Variamine Blue—II: L. ERDEY, T. MEISEL, B. MOHOS and F. TUDOS (2 *May* 1967)

Application of zone-melting technique to metal chelate systems—II. Concentration of a trace amount of metal acetylacetonate in chromium(III) acetylacetonate: HISAMITSU KANEKO, HIROSHI KOBAYASHI and KEIHEI UENO (4 *May* 1967)

Application of zone melting technique to metal chelate systems—IV. Concentration of metal-8-hydroxyquinoline chelates in 8-hydroxyquinoline: HISAMITSU KANEKO, HIROSHI KANAGAWA, HIROSHI KOBAYASHI and KEIHEI UENO (4 *May* 1967)

Spectrophotometric studies of ruthenium(III) and rhodium(III)-oximidobenzotetronic acid complexes and the simultaneous determinations of the two metals: G. S. MANKU, A. N. BHAT and D. B. JAIN (5 *May* 1967)

Redox reactions of columns: R. BELCHER, R. J. MAJER and G. A. H. ROBERTS (8 *May* 1967)

Studies on metallochromic indicators—II. Zincon and some of its metal derivatives: G. L. SINGHAL and K. N. TANDON (8 *May* 1967)

Separation and identification of some naturally occurring alkylphenanthrenes: ROLF JÖNSSON (15 *May* 1967)

LOUIS GORDON MEMORIAL AWARD

To commemorate the late Professor Louis Gordon, who was closely associated with TALANTA from its inception, the Publisher and the Editorial Board have instituted an annual Memorial Award. In view of Professor Gordon's deep interest in analytical chemistry and the presentation of scientific reports, the Award will be made to the author (or authors) of the TALANTA paper adjudged to be the best-written, stylistically, of the year. All full papers in English, French or German will be considered. The Award will take the form of a specially bound copy of the volume of TALANTA containing the paper chosen.

The Award for 1966 has been made to FOLKE INGMAN and EBBE STILL for their paper "Graphic Method for the Determination of Titration End-points" in *Talanta*, 1966, **14**, 1431.

Talanta, 1967, Vol. 14, p. i. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Photometrische Bestimmung von Kupfer mit Polyäthylenimin: MAX ZIEGLER and LÜDER ZIEGELER (6 March 1967)

Die Anwendung von Komplexbildnern in der polarographischen Analyse anorganischer Verbindungen—XIII. Polarographisches Verhalten der Komplexverbindungen des Mangans mit Mannit: JAN DOLEŽAL and OSWALD GÜRTLER (20 March 1967)

Application of isotopic exchange for the activation analytical determination of tin in nickel: M. CSAJKA (20 March 1967)

Studies in atomic fluorescence spectroscopy—V. The fluorescence characteristics and analytical determination of antimony: R. M. DAGNALL, K. O. THOMPSON and T. S. WEST (21 March 1967)

Complexation reactions of dithiocarbamates: ADAM HULANICKI (22 March 1967)

Chromatographic location and colorimetric determination of mercaptans, prolines, and free radical precursors: E. SAWICKI, C. R. ENGEL and W. C. ELBERT (23 March 1967)

Use of complex forming substances in polarographic analysis of inorganic compounds: Polarographic determination of manganese in minerals: OSWALD GÜRTLER and JAN DOLEŽAL (30 March 1967)

Mass spectrometric analysis of high purity helium and hydrogen, using a dynamic sampling and calibration system: R. T. PARKINSON (30 March 1967)

Ion-exchange behaviour of several elements in mixed solvents: T. CUMMINGS and J. KORKISCH (30 March 1967)

New titrimetric microdetermination of lanthanum: J. D. PANDEY and O. C. SAXENA (30 March 1967)

Gravimetric determination of copper(II) with *p*-amino benzoic acid: L. ERDEY, P. MARIK-KORDA and G. LIPTAY (30 March 1967)

Application of ion-associates of tris(1,10-phenanthroline)iron(II) with anions of organic dyes for sensitivity improvement of photometric iron determination: M. KNIŽEK and M. MUSILOVÁ (30 March 1967)

Polarographic behaviour of metal chelates of *o,o'*-dihydroxyazo dyes: GEORGE W. LATIMER, JR. (30 March 1967)

Successive chelatometric titration for calcium and magnesium in water with BNP: K. TÔEI and T. KOBATAKE (30 March 1967)

Studies in vanadium(IV) complexes of Azoxine S dyes: S. S. GOYAL and J. P. TANDON (30 March 1967)

Polarographic microdetermination of halogens in organic compounds after oxygen flask combustion: F. M. HABASHY, Y. A. GAWARGIOUS and B. N. FALTAOOS (30 March 1967)

Application of urease for the precipitation of nickel dimethylglyoximate by urea from homogeneous solution: SEIICHIRO HIKIME, HITOSHI YOSHIDA and MITSUHIKO TAGA (31 March 1967)

On amino-acid chromatograms obtained through development by means of ninhydrin, later studied in a hydrochloric acid medium: J. SZÁNTAY and P. SZABÓ (31 March 1967)

Oxalato compounds of tervalent thallium: A potentiometric study: S. R. SAGI and V. RAMANAK (31 March 1967)

Spectroscopic studies on scandium 8-hydroxyquinolates: TERENCE J. CARDWELL and ROBERT J. MAGEE (31 March 1967)

Selective spot test for hydrazine: T. A. LARUE (31 March 1967)

Oxidation of some sugars with copper(III): S. CHANDRA and K. L. YADAVA (1 April 1967)

Interaction of Dowex A-1 chelating resin with sparingly soluble calcium salts: E. SEGALL and G. SCHMUCKLER (4 April 1967)

Amperometric determination of neodymium(III) as tungstate: M. P. JOSHI and C. M. GUPTA (7 April 1967)

Neutron activation analysis by standard addition and solvent extraction. Determination of certain impurities in thorium and iron: A. ALIAN and R. SHABANA (12 April 1967)

New spectrophotometric method for the estimation of bismuth with EDTA: N. A. RAMAIAH, G. D. TEWARI, S. R. TRIVEDI and SARVAGYA S. KATIYAR (12 April 1967)

Studies on uranyl complexes—II. Uranyl complexes of EDTA: J. J. R. FRAÚSTO DA SILVA and M. LOURDES SADLER SIMÕES (13 April 1967)

Direct titration of glycerol by constant current potentiometry: J. R. SAND and C. O. HUBER (13 April 1967)

Fluorescent aluminium indicators derived from substituted coumarins: J. F. AGUILÁ (14 April 1967)

Co-ordinating properties of some ligand systems related to 4-(2-pyridylazo)-resorcinol: R. G. ANDERSON and G. NICKLESS (19 April 1967)

Homogeneous precipitation of basic aluminium benzoate using a buffer solution: R. J. IRVING (19 April 1967)

TALANTA MEDAL

PROFESSOR EGON STAHL

The Editorial Board of *Talanta*, has pleasure in announcing that, with the approval of the Advisory Board, the Fourth Award of the Talanta Medal (see *Talanta*, 1966, **13**, 1052) has been made to

PROFESSOR EGON STAHL

of the Institute for Pharmacognosy and Analytical Phytochemistry, University of Saarland, German Federal Republic.

Thin-layer chromatography (TLC) is simple, rapid, relatively inexpensive, versatile, and it requires very little working material. Today its use is almost routine in many organic laboratories (natural product, pharmaceutical, lipid) and the technique is becoming increasingly applied to more polar molecules. However, application of TLC mushroomed only after 1958.

Chromatography on thin layers of adsorbent was conceived as early as 1938, but its development and adoption were slow because equipment and reagents were not available commercially. These obstacles were removed by Egon Stahl, who devised a system involving standard-size glass plates, a new apparatus for preparation of thin layers, and a standard adsorbent (silica-gel-gypsum); these were presented to ACHEMA in 1958. The apparatus became commercially available from Desaga (Heidelberg) and the adsorbent from Merck (Darmstadt). Variables of the technique were studied systematically by Professor Stahl and his co-workers; they applied it to many new types of organic compound and pioneered the use of new adsorbents, which immediately became available commercially. Stahl called the method "Dünnschicht Chromatographie" or "thin-layer chromatography", which remains the most widely accepted name. His further contributions to TLC since 1958 have ensured that he remains constantly at the frontiers of its development.

Talanta, 1967, Vol. 14, p 1 Pergamon Press Ltd Printed in Northern Ireland

PUBLICATIONS RECEIVED

Laboratory Handbook of Chromatographic Methods: Editor O. MIKEŠ. Van Nostrand, London, 1966. Pp. 434. 75*s*.

An interesting book which collects together a large amount of information on all chromatographic techniques and electrophoresis. The material has been supplied by Czech authors with great experience in the field and the translation is excellent. The treatment is practical and the book will be valuable to third year students and research workers, particularly those associated with the medical and biological sciences.

Advances in Chromatography, Vols. 1, 2 and 3: Editors J. CALVIN GIDDINGS and ROY A. KELLER, Arnold, London, 1965 and 1966. Pp. XV + 392, XVI + 377 and XIII + 271. £6, £6 and 95*s*.

Each volume of this series contains a group of surveys on paper and thin-layer chromatography, electrophoresis and gas chromatography. The contributors are themselves well known workers in the fields which they discuss and their contributions contain more experimental detail than that normally found in a competent literature survey. In sections where checking was possible, the coverage was found to be complete. The series will be useful to the research worker in most fundamental and applied disciplines.

XXth International Congress of Pure and Applied Chemistry. Butterworths, London, 1965. Pp. v + 365. 75*s*.

The Congress Lectures presented in Moscow, 12–18 July 1965.

Index to Reviews, Symposia Volumes and Monographs in Organic Chemistry for the Period 1963–1964: NORMAN KHARASCH and WALTER WOLF. Pergamon, Oxford, 1966. Pp. x + 326. 105*s*.

Dynamics of Chromatography. Part 1: Principles and Theory: J. CALVIN GIDDINGS. Arnold, London, 1965. Pp. xii + 323. 90*s*.

This is a useful addition to the extensive range of books on chromatography in that it deals with the fundamental theory of the chromatographic process rather than its application. There is a very interesting section in which the "random walk" concept is applied to the theory of zone spreading. The book can be recommended to final year and post-graduate science students.

Handbuch der mikrochemischen Methoden, Vol. IV: Electronenstrahl-Mikroanalyse: HANNS MALISSA. Springer, Vienna, 1966. Pp. 154. 49 DM.

This is a comprehensive and most readable introduction to a rather new branch of analytical chemistry, and is especially welcome as the first in its field in the German language. The book is well illustrated, and has an up to date bibliography. There are chapters on Theoretical Principles of Electron Probe Microanalysis, Equipment and Applications, Measurement Techniques and Practical Examples.

NOTICE

U.S.A.

9–11 *August* 1967: **Denver X-Ray Conference on Applications of X-ray Analysis.** In or Near Denver, Colorado.

Papers are now invited on fundamental and practical applications of X-ray analysis. Technical emphasis this year is to be placed on the subject of quantitative chemical analysis by X-ray fluorescence. Titles and abstracts are due 10 April 1967 (*two* copies, please). Abstracts should be between 200 and 400 words in length. Final manuscripts (also two copies) are due 10 July. The author's written consent to publish in the copyrighted proceedings of the conference are also required at this time.

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An interesting book which collects together a large amount of information on all chromatographic techniques and electrophoresis. The material has been supplied by Czech authors with great experience in the field and the translation is excellent. The treatment is practical and the book will be valuable to third year students and research workers, particularly those associated with the medical and biological sciences.

Advances in Chromatography, Vols. 1, 2 and 3: Editors J. CALVIN GIDDINGS and ROY A. KELLER, Arnold, London, 1965 and 1966. Pp. XV + 392, XVI + 377 and XIII + 271. £6, £6 and 95*s*.

Each volume of this series contains a group of surveys on paper and thin-layer chromatography, electrophoresis and gas chromatography. The contributors are themselves well known workers in the fields which they discuss and their contributions contain more experimental detail than that normally found in a competent literature survey. In sections where checking was possible, the coverage was found to be complete. The series will be useful to the research worker in most fundamental and applied disciplines.

XXth International Congress of Pure and Applied Chemistry. Butterworths, London, 1965. Pp. v + 365. 75*s*.

The Congress Lectures presented in Moscow, 12–18 July 1965.

Index to Reviews, Symposia Volumes and Monographs in Organic Chemistry for the Period 1963–1964: NORMAN KHARASCH and WALTER WOLF. Pergamon, Oxford, 1966. Pp. x + 326. 105*s*.

Dynamics of Chromatography. Part 1: Principles and Theory: J. CALVIN GIDDINGS. Arnold, London, 1965. Pp. xii + 323. 90*s*.

This is a useful addition to the extensive range of books on chromatography in that it deals with the fundamental theory of the chromatographic process rather than its application. There is a very interesting section in which the "random walk" concept is applied to the theory of zone spreading. The book can be recommended to final year and post-graduate science students.

Handbuch der mikrochemischen Methoden, Vol. IV: Electronenstrahl-Mikroanalyse: HANNS MALISSA. Springer, Vienna, 1966. Pp. 154. 49 DM.

This is a comprehensive and most readable introduction to a rather new branch of analytical chemistry, and is especially welcome as the first in its field in the German language. The book is well illustrated, and has an up to date bibliography. There are chapters on Theoretical Principles of Electron Probe Microanalysis, Equipment and Applications, Measurement Techniques and Practical Examples.

NOTICE

U.S.A.

9–11 *August* 1967: **Denver X-Ray Conference on Applications of X-ray Analysis.** In or Near Denver, Colorado.

Papers are now invited on fundamental and practical applications of X-ray analysis. Technical emphasis this year is to be placed on the subject of quantitative chemical analysis by X-ray fluorescence. Titles and abstracts are due 10 April 1967 (*two* copies, please). Abstracts should be between 200 and 400 words in length. Final manuscripts (also two copies) are due 10 July. The author's written consent to publish in the copyrighted proceedings of the conference are also required at this time.

OBITUARY

It is with regret that we announce the death in Prague, on 27th March 1967 at the age of 76, of JAROSLAV HEYROVSKÝ. Formerly Head of the Division of Physical Chemistry of Charles University in Prague, Professor Heyrovský is well known for his invention and pioneer development of polarography and polarographic analysis, for which he was awarded the Nobel Prize in 1959.

Readers of *Talanta* will recall that Professor Heyrovský's seventy-fifth birthday (December 1965) was honoured by publication of a special issue of the journal, comprized entirely of invited contributions from his former students and associates

The Czechoslovak Academy of Sciences has lost one of its best members, and the Polarographic Institute in Prague its first (and eponymous) director

ADVISORY BOARD OF TALANTA

The Editorial Board and Publishers of *Talanta* take pleasure in welcoming the following new members to the Advisory Board of the journal

T. HADJIIOANNOU G. TÖLG

THEMISTOCLES HADJIIOANNOU (Greece) was born in 1927 and studied at University of Thessaloniki. In 1960 he received his Ph.D. at University of Illinois, where he subsequently became Assistant Professor. He is currently Director of the Laboratory of Analytical Chemistry at University of Athens. His research interests include spectrophotometric titrations, isomation techniques, ion specific transducers, complexometry, and trace analysis by catalytic methods.

Born in 1929, GÜNTHER TÖLG (German Federal Republic) received his education in chemistry at Johannes Gutenberg-University in Mainz. He became Diplomchemiker in 1956 and Dr. rer. nat. in 1959 under Professor W. Geilmann. Since 1965 he has been Dozent of Analytical Chemistry at Mainz. His research activities are in organic and inorganic trace- and ultramicroanalysis, especially development of accurate methods for determination of extremely small amounts of elements in organic compounds and materials and investigation of the animal metabolism of pesticides.

Talanta, 1967, Vol. 14, p. i. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Ein Schnellverfahren zur Rheniumbestimmung in Molybdänit: L. BALABANOFF, F. BERNASCONI H. LARA and R. WOERNER. (25 *November* 1966)

Determination of uranium in electro-refined plutonium by a combined ion-exchange X-ray fluorescenc e technique: J. A. HAYDEN (18 *January* 1967)

A high-speed micro-vacuum fusion apparatus: M. T. LILBURNE (23 *January* 1967)

Present state of complexometry—IV. Determination of rare earths: RUDOLF PRIBIL (23 *January* 1967)

End-point sharpness in thermometric titrimetry: H. J. V. TYRRELL (23 *January* 1967)

Determination of trace amounts of sulphur in selenium: BRITT-LOUISE SJÖBORG (24 *January* 1967)

Critical micelle concentration determination of non-ionic surfactants by electrocapillary curves: WAHID U. MALIK, PURAN CHAND and S. M. SALEEM (26 *January* 1967)

Polarographic reduction behaviour of clay minerals: WAHID U. MALIK and G. C. GUPTA (26 *January* 1967)

Aspects of the precipitation of nickel dimethylglyoximate: S. J. LYLE and R. MAGHZIAN (27 *January* 1967)

Determination of radioactive cobalt in reactor coolant water by solvent extraction: KENJI MOTOJIMA, SHOJI BANDO and NORI TAMURA (30 *January* 1967)

Separation of copper and iron in their different valency states by paper chromatography: P. B. JANARDHAN and AGNES PAUL (31 *January* 1967)

Reactions of Eriochrome Blue Black R: G. L. SILVER and R. C. BOWMAN (2 *February* 1967)

Polarographic behaviour of Mo(VI) in aspartic acid and its determination: C. M. GUPTA and J. K. GUPTA (2 *February* 1967)

Spectrophotometric determination of chromium with Xylenol Orange and Methylthymol Blue: K. L. CHENG (3 *February* 1967)

Analytical method for the determination of ^{3}H and ^{85}Kr in aqueous samples by liquid scintillation techniques: J. B. COHEN, J. L. SETSER, W. D. KELLEY and S. D. SHEARER, JR. (4 *February* 1967)

Decomposition of thiosulphate in acidified oxidants: G. W. LATIMER, JR. and ELAINE I. STETEKO (4 *February* 1967)

Determination of barium in sea water by a cation-exchange concentration procedure: BARNEY J. SZABO and OIVA JOENSUU (4 *February* 1967)

Microchemical detection of isocyanides: E. V. CRABTREE, E. J. POZIOMEK and D. J. HOY (4 *February* 1967)

Gas-chromatographic examination of organophosphorous pesticides and their oxidation products: J.RUZICKA, J. THOMSON and B. B. WHEALS (6 *February* 1967)

Solvent extraction of amine complexes: M. KYRŠ and M. PIVŮNKOVÁ (8 *February* 1967)

APDC-MIBK extraction system for the determination of trace elements in saline waters by atomic-absorption spectrophotometry: ROBERT R. BROOKS, BOB J. PRESLEY and ISAAC R. KAPLAN (8 *February* 1967)

Promethazine hydrochloride as a new redox indicator in vanadametry: H. SANKE GOWDA, R. SHAKUNTHALA and P. G. RAMAPPA (8 *February* 1967)

Titrimetric, coulometric and spectrophotometric determination of manganese following perchloric acid oxidation in the presence of pyrophosphate: JOHN KNOECK and HARVEY DIEHL (9 *February* 1967)

Some solvent effects on the solvent extraction of 8-quinolinol: HORACIO A. MOTTOLA and HENRY FREISER (9 *February* 1967)

Determination of molybdenum in the soil solution by neutron-activation method: W. ŻMIJEWSKA and J. MINCZEWSKI (10 *February* 1967)

Application of thermoelectric potential measurements in chemical analysis—II. Determination of aluminium in iron alloys: A. KRAJINI and J. DOLEŽAL (13 *February* 1967)

Polarographic study of inhibitors and catalysts for the reaction of dissolved oxygen with sulphite ion: Y. ISRAEL, A. VROMEN and B. PASCHKES (13 *February* 1967)

Separation and acid equilibria of Xylenol Orange and Semixylenol Orange: MITSUMASA MURAKAMI, TAKASHI YOSHINO and SHIRO HARASAWA (15 *February* 1967)

Talanta, 1967, Vol. 14, p. i. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Study of iron(II)–iron(III) behaviour during iron(II) oxide determinations: J. C. VAN LOON. (16 *December* 1966)

Anion-exchange separation of cobalt from nickel and its electro-deposition: O. G. BALAKRISHNAN NAMBIER and P. R. SUBBARAMAN. (23 *December* 1966)

Oxidimetric determination of indigo with iron(III) and hexacyanoferrate(III): G. GOPALA RAO and V. RUKMINI. (23 *December* 1966)

A new reductimetric reagent: iron(II) in a strong phosphoric acid medium—V: G. GOPALA RAO and V. RUKMINI. (23 *December* 1966)

A new oxidimetric reagent: Potassium dichromate in a strong phosphoric acid medium—VIII. Potentiometric determination of molybdenum(VI) and vanadium(V): G. GOPALA RAO and U. MURALIKRISHNA. (23 *December* 1966)

Reduction of iridium after oxidation in fuming perchloric acid: E. JACKSON and D. A. PANTONY. (23 *December* 1966)

Studies in atomic-fluorescence spectroscopy—III. Microwave electrodeless discharge tubes as spectral sources for atomic-fluorescence and atomic-absorption spectroscopy: R. M. DAGNALL, K. C. THOMPSON and T. S. WEST. (23 *December* 1966)

Studies in atomic-fluorescence spectroscopy—IV. The atomic-fluorescence spectroscopic determination of selenium and tellerium: R. M. DAGNALL, K. C. THOMPSON and T. S. WEST. (23 *December* 1966)

Separation of ions by alteration of the concentration of the ligand in a discontinuous countercurrent extraction system: C. R. BOSWELL and R. R. BROOKS. (29 *December* 1966)

Mass spectrometry of metal chelates—I. Detection on the picogram scale: A. E. JENKINS and J. R. MAJER. (5 *January* 1967)

Spectrophotometric extractive titrations—IV. Determination of zinc in germanium dioxide and in germanium chloride: AFTANAS GALÍK. (5 *January* 1967)

Precipitation of bismuth basic acetate from homogeneous solution: P. F. S. CARTWRIGHT. (5 *January* 1967)

Metal chelate exchange in the organic phase—I. Theory. Application in spectrophotometry and complex chemistry: JAROMÍR RŮŽIČKA and JIŘÍ STARÝ. (5 *January* 1967)

Spectrophotometric determination of osmium with ammonium thiocyanate: MOHSIN QURESHI and KISHORE N. MATHUR. (5 *January* 1967)

Solvent extraction of indium with 1-(2-pyridylazo)-2-naphthol. The formation of mixed complexes: YU. A. ZOLOTOV, I. V. SERYAKOVA and G. A. VOROBYEVA. (10 *January* 1967)

Some vanadium(V) complexes as reagents for the photometric determination of alcohols: MOTOHARU TANAKA and ISAO KOJIMA. (11 *January* 1967)

Polarographic study of bis-(2-pyridyl)-disulphide di-*N*-oxide and bis(2-quinolyl)-disulphide di-*N*-oxide in aqueous ethanol: I. EL-KHIAMI and R. M. JOHNSON. (11 *January* 1967)

Alloy electrodes in potentiometry—I. Study of platinum—20% rhodium electrode in redox and acid-base titrations: V. T. ATHAVALE, R. G. DHANESHWAR and D. A. SARANG. (19 *January* 1967)

Sorption of hydrolytic products of iron(III), aluminium(III) and chromium(III) on the silica column, and its analytical use: F. VYDRA and J. GALBA. (19 *January* 1967)

Talanta, 1967, Vol. 14, p. i. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Radiochemische Trennungen mit Hilfe der Ringofenmethode II: Das System $^{99}Mo/^{99}Tc$: D. KLOCKOW (10 *November* 1966)

Determination of microgram quantities of tin(IV) by a combined ion-exchange/X-ray fluorescence technique: B. R. CHAMBERLAIN and R. J. LEECH (21 *November* 1966)

Separation of tin from other elements by partition chromatography: J. S. FRITZ and G. L. LATWESEN (21 *November* 1966)

1-Hydroxy-ethylidene-1,1-diphosphonic acid as a volumetric and masking agent: R. PŘIBIL and V. VESELÝ (22 *November* 1966)

Separation of As(V) and As(III) by thin-layer chromatography: K. OGUMA (23 *November* 1966)

Instrumental activation analysis of vegetable tissue: E. STEINNES (23 *November* 1966)

Estimation of the minimum detectable concentration and optimum instrumental conditions in precison absorption spectrophotometry of molecules in the condensed phase: J. J. CETORELLI and J. D. WINEFORDNER (23 *November* 1966)

Fluorimetric determination of sebacic acids: ZBIGNIEW GREGOROWICZ and PIOTR GÓRKA (25 *November* 1966)

Kinetics of the precipitation of palladium dimethylglyoximate from homogeneous solution: PAUL R. ELLEFSEN and LOUIS GORDON (1 *December* 1966)

Computer calculation of equilibrium concentrations in mixtures of metal ions and complexing species: D. D. PERRIN and I. G. SAYCE (2 *December* 1966)

Substoichiometric determination of traces of gold by radioactive isotope-dilution analysis: D. A. BEARDSLEY, G. B. BRISCOE, J. RŮŽIČKA and M. WILLIAMS (2 *December* 1966)

Spectrophotometric determination of cobalt using phenanthrenequinone monoxime as analytical reagen t K. C. TRIKHA, MOHAN KATYAL and R. P. SINGH (6 *December* 1966)

Some aspects of the reactions between selenium-containing ligands and platinum group metals: L. S BARK and D. BRANDON (6 *December* 1966)

Physico-chemical and analytical study of thallous chelates with hydroxy-phenols: O. S. TOMAR and P. D. BRATTACHARYA (6 *December* 1966)

Inorganic polarography in organic solvents—III. Analytical applications of metal–acetylacetone complexes in toluene: B. K. AFGHAN, R. M. DAGNALL and K. C. THOMPSON (6 *December* 1966)

Extractive photometric determination of lanthanides and yttrium with chlorophosphonazo DAL: BŘETISLAV BUDĚŠINSKÝ and BLANKA MENCLOVÁ (6 *December* 1966)

Complexometric determination of iron (III) with 2-hydroxy-1-naphthaldoxime as indicator: V. B. S. CHAUHAN (7 *December* 1966)

Emission spectra of nitrous oxide supported acetylene flames at atmospheric pressure: G. F. KIRKBRIGHT M. K. PETERS and T. S. WEST (8 *December* 1966)

New method for the determination of sorbic acid: P. SPACU and H. DUMITRESCU (8 *December* 1966)

New method for the determination of pentachlorophenol by atomic absorption spectrophotometry: Y. YAMAMOTO, T. KAMAMARU and Y. HAYASHI (9 *December* 1966)

Determination of calcium by atomic-absorption spectrophotometry combined with extraction: MASAAKI YANAGISAWA, MASAMI SUZUKI and TSUGIO TAKEUCHI (13 *December* 1966)

Determination of selenium snf tellurium in silver chloride and uranium oxide: B. G. RUSSELL W. V. LUBBE, ANITA WILSON, ELAINE JONES, J. D. TAYLOR and T. W. STEELE (20 *December* 1966)

Electron microscopy and diffraction studies on coprecipitation—I. Morphological study on coprecipitation: KAZUYOSHI TAKIYAMA and LOUIS GORDON (20 *December* 1966)

Talanta, 1967, Vol. 14, p. i. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Purification of Laboratory Chemicals: D. D. PERRIN, W. L. F. AMAREGO and DAWN R. PERRIN. Pergamon, Oxford, 1966. Pp. viii + 362. 70*s*.

An account is given of the techniques available for purification of chemical compounds, and this is followed by a collection of instructions for purifying individual compounds (arranged alphabetically and classified as organic and inorganic). The last chapter deals with purification of classes of compounds.

History of Analytical Chemistry: FERENC SZABADVÁRY. Pergamon, Oxford, 1966. Pp. ix + 419. £6.

This volume will prove invaluable to historians of science and to all chemists interested in the origins of analytical chemistry and the lives of the great analysts of the past. It would not be surprising if it germinated fresh ideas in the minds of modern analysts.

Spot Tests in Organic Analysis: FRITZ FEIGL. Elsevier, Amsterdam, 7th Ed., 1966. Pp. XXIII + 772. 170*s*.

The latest edition of this well-known work is a completely revised and reorganised text, containing substantially more material than the last edition, much of it being work published for the first time. New features are sections on the differentiation of isomers and the detection of particular structures or types of compound.

Progress in Nuclear Energy, Series IX—Analytical Chemistry, Vol. 4: Eds. C. E. CROUTHAMEL, D. C. STEWART and H. A. ELION. Pergamon, Oxford, 1966. Pp. v+ 166. 70*s*.

This volume of the series is mainly concerned with developments in nuclear methods of analysis that are more physical than chemical. It contains reviews of solid state charged particle detectors (N. J. Hansen), advances in neutron activation analysis (V. P. Guinn), slow electron interaction with adsorbed gases (D. Lichtman and R. B. McQuistan) and the use of neutron generators in activation analysis (J. E. Strain). The reviews provide critical surveys of their subject until 1964 and some of the references are usefully annotated.

Progress in Nuclear Energy, Series IX—Analytical Chemistry, Vol. 6: Eds. D. C. STEWART and H. A. ELION. Pergamon, Oxford, 1966. Pp. v + 260. 90*s*.

This volume contains reviews of ion-exchange in mixed and non-aqueous media (J. Korkisch), neutral bifunctional organophosphorus compounds as solvent extractants (J. W. O'Laughlin), anion-exchange in nitrate solutions (J. Faris and R. F. Buchanan), and the analytical chemistry of neptunium (G. A. Burney, E. K. Dukes and H. J. Groh) and polonium (R. C. Lange). The articles are critical, contain a lot of useful data and complement each other to a fair degree. The typographical standard of the series is maintained.

NOTICE

U.S.A.

21–23 *June* 1967: **Analytical Summer Symposium devoted to "Modern Titrimetry":** Sponsored jointly by the Analytical Division of ACS and the journal *Analytical Chemistry*.

Further information about the programme may be obtained from Joseph Jordan (212 Whitmore Laboratory, Pennsylvania State University, University Park, Pa. 16802). Inquiries concerning local arrangements should be directed to Alvin L. Beilby (Department of Chemistry, Pomona College, Claremont, California 91713).

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PUBLICATIONS RECEIVED

Electronic Electrochemical Measuring Instruments: D. DOBOS, TERRA, Budapest, 1966. Pp. 449. 105*s*.

This is a readable and valuable reference book, half of which covers the theory of basic electronics and the design of the most important circuit elements, with notes on their application in methods of measurement. The design of pH meters, conductometers, h.f. oscillometers, polarographs and coulometers is discussed with reference to commercially available equipment. A useful few pages on care of electronic instruments should be compulsory reading for all students. The second half of the book is an international compendium of electronic electrochemical measuring instruments, with many photographs, diagrams and technical details. The information here should be of considerable interest to anyone faced with the problem of choosing new laboratory equipment.

Protides of the Biological Fluids: Vol. 14 of a Series on Proteins and Related Subjects: Proceedings of the 14th Colloquium at Bruges in 1966: Editor, H. PEETERS. Elsevier, 1967. Pp. xiii + 734. £12.

The subject matter falls into four divisions, namely, metal-binding proteins (26 papers), protein level and turnover (30 papers), determination of protein structure by physical methods (6 papers), separation techniques (31 papers) and, in addition to an introductory lecture by E. F. Lüscher on "The Biochemical Properties and the Biological Function of Fibrinogen", there are six other papers. Most papers are in English but there are a few in German and French. In the section on separation techniques particular emphasis, not surprisingly, is on the use of gel-filtration. The book is well-produced, with many illustrations and tables, and the editor is to be congratulated on the speed with which the papers have been published. While primarily the book is of value to those working in the protein field there are details of methods of value to other research workers.

NOTICE

16–18 *September* 1968

Fifth International Symposium on Chromatography and Electrophorese. Organized by the Belgian Society of Pharmaceutical Sciences, Brussels.

The official languages will be French, Dutch, English and German, and a scientific exhibition will be held during the Symposium.

Further information from: The Secretary's Office, The Belgian Society of Pharmaceutical Sciences, 11 rue Archimede, Brussels 4.

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PAPERS RECEIVED

Le dosage du plomb dans les eaux alimentaires par trois methodes polarographiques: M. DEVALERIOLA and P. NANGNIOT. (4 *July* 1967)

Polarographische Bestimmung des Schwefels in Benzin: H. HOLZAPFEL and K. SCHÖNE. (3 *August* 1967)

Determination of moisture on thorium dioxide by a coulometric electrolytic measurement with electronic integration: E. A. SCHAFFER and J. O. HIBBITS. (11 *August* 1967)

Chromatographic separation of diastereoisomeric esters. II. Mandelates and lactates of 2-methylbutanol-1, 3-methylbutanol-2, pentanol-2 and hexanol-2: R. E. LEITCH, H. L. ROTHBART and WILLIAM RIEMAN III. (15 *August* 1967)

Metal ion separations using cellulose phosphate as an ion-exchanger: DONALD H. SCHMITT and JAMES S. FRITZ. (21 *August* 1967)

Application of 2-diphenylacetyl-1,3-indandione chemistry in the identification of organic compounds: W. A. MOSHER, E. J. POZIOMEK and I. S. BECHARA. (22 *August* 1967)

Improved method for the simultaneous absorptiometric determination of cobalt and nickel with quinoxaline-2,3-dithiol: J. A. W. DALZIEL and A. K. SLAWINSKI. (25 *August* 1967)

Note on the separation and determination of certain 17-ketosteroids from human urine: S. K. WAHBA, S. W. AMIN, M. HASSAN and A. A. EL-DAMATY. (25 *August* 1967)

Studies on Methymol Blue—I. Separation and purification of Methylthymol Blue and Semi-Methylthymol Blue: TAKASHI YOSHINO, HARUMI IMADA, TADAYOSHI KUWANO and KATSUYA IWASA. (25 *August* 1967)

Studies on metallochromic indicators—III. Hematoxylin and hematein as metallochromic indicators: G. K. SINGHAL and K. N. TANDON. (29 *August* 1967)

The masking coefficient in precipitation reactions: D. E. RYAN. (29 *August* 1967)

Substoichiometric determination of tungsten in steel by neutron-activation analysis: R. A. NADKARNI and B. C. HALDAR. (30 *August* 1967)

Anion-exchange separation of metal ions in dimethyl sulphoxide-methanol-hydrochloric acid: JAMES S. FRITZ and MARCIA LEHOCZKY GILLETTE. (31 *August* 1967)

Application of polarography and related electroanalytical techniques to the determination of derivatives of dithiocarbamic acid—I. Sodium diethyldithiocarbamate: M. J. D. BRAND and B. FLEET. (1 *September* 1967)

Application of polarography and related electroanalytical techniques to the determination of derivatives of dithiocarbamic acid—II. Tetramethylthiuram disulphide: M. J. D. BRAND and B. FLEET. (1 *September* 1967)

Application of polarography and related electroanalytical techniques to the determination of derivatives of dithiocarbamic acid—III. Ethylene *bis*dithiocarbamates: M. J. D. BRAND and B. FLEET. (1 *September* 1967)

Arsenazo III and analogues—I. Concerning the electronic structure of arsenazo III in various acidic media: S. B. SAVVIN and E. W. KUZIN. (4 *September* 1967)

Arsenazo III and analogues—II. Concerning the complexing of niobium with reagents containing the *o*, *o*-dioxyazo grouping: T. P. ALIMARIN, S. B. SAVVIN and L. A. OCHANOVA. (4 *September* 1967)

α-Oximinoacetoacetarylamides as analytical reagents for palladium: S. B. PATEL, M. R. PATEL and B. N. MANKAD. (4 *September* 1967)

A new concept of automated radiochemical analysis based on substoichiometric separation: J. RŮŽIČKA and C. G. LAMM. (4 *September* 1967)

Determination of nitrogen in an aluminium-killed steel by an isotope dilution method using $Al^{15}N$: KEIICHI FURUYA, SHOICHIRO OKUYAMA, SATOSHI TACHIKAWA and HITOSHI KAMADA. (5 *September* 1967)

The role of 70–80% perchloric acid as oxygen donor and determination of oxidation potentials made available: G. FREDERICK SMITH. (8 *September* 1967)

Extraction of radiogold and radiomercury and some other radioisotopes with mesityl oxide: A. ALIAN. (12 *September* 1967)

Solvent extraction of chromium(III), molybdenum(VI) and tungsten(VI) with thenoyltrifluoroacetone: ANIL K. DE and CHITTARANJAN SAHU. (12 *September* 1967)

Solvent extraction and photometric determination of molybdenum: A. I. BUSEV and T. V. RODIONOVA. (15 *September* 1967)

Exchange reactions on volumes: G. A. H. ROBERTS. (20 *September* 1967)

Photometric and spectrochemical determination of gold in copper, lead, and iron pyrites concentrates, after preliminary separation by extraction: N. JORDANOV, ST. MAREVA, N. KRASNOBAEVA and N. NEDYALKOVA. (21 *September* 1967)

Zur polarographie der n-Butyl-zinnchloride: K. ISSLEIB, H. MATSCHINER and S. NAUMANN. (15 *September* 1967)

Talanta, 1967, Vol. 14, p. ii. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Flame Photometry Theory: E. PUNGOR. Van Nostrand, London, 1967. Pp. xi + 200. 60s.

This monograph gives a concise survey of the theories of flame velocity and propagation, reactions in the flame, and atomization. The problems of temperature measurement are also dealt with. There are a large number of graphs which complement the many equations and illustrate clearly the principles expounded. The analytical chemist will benefit greatly by studying the work.

Tungsten and its Compounds: G. D. RIECK. Pergamon, Oxford, 1967. Pp. 138. 45s.

In spite of the vast quantity of information presented, the book is readable. The references cited are adequate to provide an intending researcher with a modern basis for a literature search. At the same time this neat monograph provides an excellent introduction to a broad area of investigation, and interest is added by the author's references to the applications and uses of various compounds.

Lyuminestsentnii Analiz Neorganicheskikh Veshchestv: E. A. BOZHEVOLNOV. Izdat. "Khimia", Moscow, 1966. Pp. 416. 1 Rb. 89 Kop.

This book contains an account of the theory and practice of luminescent analysis of inorganic substances. The apparatus and techniques are described, and available reagents and the development of new ones are discussed. Detailed methods are given for elements in groups I–VIII of the periodic table.

Khemilyuminestsentnii Analiz: A. K. BABKO, L. I. DUBOVENKO and N. M. LUKOVSKAYA. Izdat. "Tekhnika", Kiev, 1966. Pp. 250. 96 Kop.

The fundamentals of the phenomenon of chemiluminescence are expounded, and the properties of the most important components of chemiluminescent reactions are described. An account is given of the use of chemiluminescence for the titrimetric determination of 10^{-6}–10^{-9} g of substances, on the basis of their catalytic or inhibiting capacity. The use of this method for the analysis of several ultra-pure materials is described.

Arsenazo III: Metodi fotometricheskogo opredelenya redkikh i aktinidnikh elementov: S. B. SAVVIN. Atomizdat, Moscow, 1966. Pp. 256. 93 Kop.

The theory and practice of the use of Arsenazo III and its analogues for the determination of Th, U, Zr, Hf, Sc, Ce, La, Nb, Sr, Ba, S, lanthanides and actinides are described. The mechanism of the complex formation and the nature of the colour reactions, the composition and structure of the complexes, and the selectivity and other properties of the reagents in this series are all discussed. Full details are given of the methods of determining elements in various materials by this method.

Radiometric Titrations: T. BRAUN and J. TÖLGYESSY. Pergamon, Oxford, 1967. Pp. x + 168 55s.

The monograph is a very clear and comprehensive account of the subject. The exposition is greatly enhanced by the frequent use of diagrams and photos, which show titration curves and apparati. The method, which holds out the possibility of determining microgram amounts of many ions with a relative precision of 1% is of considerable interest. The interest, modest price and quality of production should make it popular with many analysts.

Chromatographic Reviews, Volume 8: Ed. MICHAEL LEDERER, Elsevier, Amsterdam, 1966. Pp. viii + 298. £5. 10s.

This volume continues the task of its predecessors by providing competent and detailed reviews in various aspects of chromatography. The first three articles are on gas chromatography and deal with the flow of gases in porous media, the study of pyrolysis products and trace analysis. An interesting article outlines chromatography and electrophoretic techniques for the separation of denaturation and degraded fibrous proteins. Elsewhere there are reviews on the chromatography of triglycerides, lipids and co-ordination compounds and one on the use of papers impregnated with ion exchangers. This is the last annual volume to appear, henceforth it is the intention of the editor to publish the review twice or thrice a year.

Talanta, 1967, Vol. 14, p. ii. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

POLAND

10–15 *September* 1968: **Third Polish Analytical Conference,** Warsaw Polytechnic, Warsaw.

The main subjects to be dealt with are: basic problems of analytical chemistry, analytical methods in organic and inorganic industry, and technique of analytical chemistry. Papers on these subjects (in English, French, German or Russian) may be submitted not later than 30 September 1967. Address all correspondence to Dr. A. Hulanicki, Warszawa 22, ul. Pasteura 1, Poland.

U.S.A.

8–10 *November* 1967: **The 9th Eastern Analytical Symposium,** Statler-Hilton Hotel, New York City. (Sponsored by the Analytical Groups of the New York and North Jersey Sections of the American Chemical Society; the Baltimore-Washington, Delaware Valley, New York, and New England Sections of the Society for Applied Spectroscopy; and the American Microchemical Society).

For further information contact Mr G. L. Davis, Dalare Associates, 2300 Locust Street, Philadelphia, Pa. 19103, U.S.A.

3–8 *March* 1968: **The Nineteenth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy,** Penn-Sheraton Hotel, Pittsburgh, Pennsylvania, U.S.A.

An estimated 300 papers on all phases of Analytical Chemistry and Spectroscopy will be presented. The theme will be Analytical Chemistry and Spectroscopy for the Future. Symposia on 11 other subjects are now being arranged. Papers are not restricted to the symposium subjects and original papers on all phases of analytical chemistry and spectroscopy are invited. Prospective authors should submit three copies of a 150 word abstract to: Dr. John O. Frohliger, Department of Occupational Health, Graduate School of Public Health, University of Pittsburgh, Pittsburgh, Pennsylvania, 15213, U.S.A. by 15 October 1967. In addition to the programme of technical papers, there will be an exhibition of the newest analytical instrumentation.

ERRATUM

D. BETTERIDGE: Extractive indicators in complex-formation titrations—theory and practice. *Talanta* 1966, **13**, 1497.

Equation (12) on p. 1500 should read:

$$\alpha_{2(D)} = K_{a1} \cdot K_{a2} / \left\{ [H^+]^2 + [H^+]K_{a1}\left(1 + K_{DR}\frac{V_{org}}{V_{aq}}\right) + K_{a1}K_{a2} \right\}.$$

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Talanta, 1967, Vol 14, p 11 Pergamon Press Ltd Printed in Northern Ireland

PAPERS RECEIVED

Application des courbes de volatilisation–excitation à la détermination des conditions de l'analyse spectrochemique de l'oxyde de tantale: J BRIL and J. VINOT. (16 *January* 1967)

Spektrophotometrische Bestimmung von Wolfram in Molybdän: B NEEF and H -G DOGE. (7 *February* 1967)

Studies on the polarographic maxima of amido black: SUDARSHAN LAL and S. N. SRIVASTAVA. (16 *February* 1967)

Interference of the ammonium ion in Mohr's method for the determination of chloride: JACOB BLOCK and OSCAR B. WATERS, JR. (20 *February* 1967)

Determination of trace amounts of calcium, magnesium, iron and nickel in aluminium salts by atomic-absorption spectrophotometry with a microwave-excited source and hollow-cathode lamps: G. B. MARSHALL and T S. WEST. (20 *February* 1967)

Critical review of methods of isolating and separating the noble metals—II: F E. BEAMISH. (23 *February* 1967)

Explosion hazards with xenon trioxide solutions ("xenic acid"): JOHN H. HOLLOWAY. (23 *February* 1967)

Thorium free ammonium hexanitratocerate: G F SMITH. (24 *February* 1967)

Cation-exchange behaviour of several elements in nitric acid–organic solvent media: J. KORKISCH, F. FEIK and S. S. AHLUWALIA. (27 *February* 1967)

Radiochemical separation of strontium by isotopic exchange: I. H. QURESHI, M. S. SHAHID and S. M. HASANY (27 *February* 1967)

Interference Index: L. DE GALAN. (28 *February* 1967)

Radioactive isotope-dilution procedure for the determination of rare earth metals: G. B. BRISCOE and A. DODSON. (1 *March* 1967)

Homogeneous nucleation of magnesium hydroxide: DAVID H. KLEIN, MELVIN D. SMITH and JAMES A. DRIY. (1 *March* 1967)

Chromogenic reactions of zirconium with Solochrome Black T: T. C. SHARMA and O. P. SINHA (1 *March* 1967)

The meaning of "sensitivity" in trace analysis: J. E. BARNEY II (3 *March* 1967)

Eléments de fluorimétrie organique fonctionelle: M. PESEZ and J. BARTOS. (3 *March* 1967)

Study of the niobium-1-(2-pyridylazo)-2-naphthol (PAN) reaction: ELSIE M. DONALDSON and W. R. INMAN. (3 *March* 1967)

Interfacial free energies of ionic crystals: G. CLEGG and T P. MELIA. (6 *March* 1967)

Elektronisches Rechnen in der Analytischen Chemie—III. ALGOL-Prozeduren zur Korrelations-rechnung: G. GOTTSCHALK. (7 *March* 1967)

Spectrophotometric determination of hexafluoroarsenate with ferroin: VERNON S ARCHER and FRANKLIN G. DOOLITTLE. (8 *March* 1967)

Spectroscopy in separated flames—I. The use of the separated air–acetylene flame in thermal emission spectroscopy: G F KIRKBRIGHT, A SEMB and T. S WEST (15 *March* 1967)

Talanta, 1967, Vol. 14, p. ii. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Instrument and Chemical Analysis Aspects of Electron Microanalysis and Macroanalysis: H. A. ELION. Pergamon, Oxford, 1966. Pp. 252. 90*s*.

This is a useful review, more suited to the worker with some experience in the field, though the attempt to cover every possibility and aspect of the topic renders the book rather heavy reading. A useful set of tables and list of original references will be of value to the researcher. There are chapters on Electron Optics, X-Ray Optics, X-Ray Detectors and Detection, Specimen Preparation and Observation, Quantitative X-Ray Emission Analysis, and Future Developments.

Pharmaceutical Analysis, Vol. 1, Theory and Application: ed. L. G. CHATTEN. Arnold, London, 1966. Pp. xii + 504. 115*s*.

This is the first of two volumes and deals with the theory and practice of the more common non-instrumental techniques of pharmaceutical analysis, each section being compiled by an expert in the field. The theoretical treatment is reasonably limited and is supported by adequate practical detail, especially of technique, and by comprehensive lists of references to applications. The very full index to analytical procedures for a large number of compounds will be extremely useful to students, professional pharmaceutical analysts and research workers alike.

Rapid Methods of Trace Analysis for Geochemical Application: R. E. STANTON. Arnold, London, 1966. Pp. vii + 96. 25*s*.

This little book is a compilation of the methods that have been found to give rapid trouble-free estimation of traces of elements in geochemical survey work. The methods are designed for use in the field and permit the completion of as many as 100 determinations a day. The precision ranges from 10 to 25%, depending on the method and on the skill of the operator, but this is acceptable for the type of work. There are useful sections on reagents, statistics, and decomposition of samples, as well as the main section on the procedures themselves.

Atomic-Absorption Spectrophotometry, 2nd (revised) edition: W. T. ELWELL and J. A. F. GIDLEY. Pergamon, Oxford, 1966. Pp. ix + 140. 42*s*.

This book has been thoroughly brought up to date and fully maintains the standard set by its first edition. It is an essential in the library of anyone working in this field, and can strongly be recommended to students and those contemplating the use of atomic-absorption methods.

ERRATA

M. R. F. ASHWORTH and G. BOHNSTEDT: Reagent for the detection and determination of *N*-active hydrogen, *Talanta* 1966, **13**, 1631–1635.

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Tautomer linking signs (⇅) were used instead of resonance structure linking signs (↕) in equations (2)–(4).

H. N. ELSHEIMER: Complexometric determination of gallium with Calcein Blue as indicator, *Talanta*, 1967, **14**, 97–102.

The acknowledgement should include a statement that the work was done at the Dow Chemical Company, Rocky Flats Division, Box 888, Golden, Colorado 80402.

H. C. HOLLIFIELD and J. D. WINEFORDNER: Fluorescence and phosphorescence characteristics of anticoagulants, *Talanta*, 1967, **14**, 103–107.

In Table I on p. 105, the limits of detection (L. of D.) should be expressed in *μg/ml*, and not in *mg/ml*.

EDITORIAL NOTICE

Authors in United States and Canada

SINCE Professor Gordon's untimely death robbed this journal of one of its most devoted servants, Mr. HOWARD FRANCIS JR. has carried on as sole Regional Editor for the Western Hemisphere and has joined the Editorial Board. We are glad to announce that Professor J. S. FRITZ has accepted our invitation to collaborate with Mr. Francis in this work. We take the opportunity to remind authors that because of the large number of papers submitted to *Talanta* from the United States and Canada, publication will be facilitated if manuscripts are sent direct to either of these two Regional Editors, who will arrange for rapid refereeing within the Western Hemisphere. Responsibility for final acceptance and editing remains, of course, with the Editor-in-Chief and the Editorial Board.

Mr. H. J. FRANCIS, JR.
Analytical Department
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J. Am. Chem. Soc., 1923, **45**, 1423.

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NOTICE

U.S.A.

October 9–12, 1967. **Association of Official Analytical Chemists, 81st Annual Meeting,** Marriott Motor Hotel, Twin Bridges, Washington, D.C. Contact LUTHER G. ENSMINGER, Association of Official Analytical Chemists, Box 540. Benjamin Franklin Station, Washington, D.C. 20044."

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PUBLICATIONS RECEIVED

The Analysis of Nickel: C. L. LEWIS, W. L. OTT and N. M. SINE. Pergamon, Oxford, 1966. Pp. x + 214. 55*s*.

This book gives a thorough account of the classical and instrumental methods available for the determination of impurities in nickel metal. Some of the methods are also applicable to the analysis of nickel alloys, but only if the alloy is almost all nickel. The standards of this series are fully maintained.

Handbook of Physical Constants: SYDNEY P. CLARK, JR., Editor. Revised Edition, Geological Society of America, New York, 1966. Pp. vii + 587. $8.75.

This reference book is a compilation of the physical constants required by geologists, geophysicists and geochemists. The material presented in the first edition in 1942 has been thoroughly brought up to date and has been considerably expanded. Analysts working in the ceramic, cement and silicate industries or in geological and geochemical exploration, may find it very useful.

Elementary Practical Organic Chemistry, Part 2: Qualitative Organic Analysis: ARTHUR I. VOGEL. 2nd Edition, Longmans, London, 1966. Pp. xv + 431. 35*s*.

The most important change from the first edition is the inclusion of a chapter on spectroscopic methods of identification. This chapter covers the use of ultraviolet, visible and infrared spectroscopy, mass spectrometry, and nuclear magnetic resonance, and in the present state of development of analysis is undoubtedly the most useful and timely section of the book. The use of quantitative information as an aid to qualitative identification is also a feature that commends the book for student use.

Mass Spectrometric Analysis of Solids: ARTHUR J. AHEARN, Editor. Elsevier, Amsterdam, 1966. Pp.175. 60*s*.

An excellent review of the present state of spark source mass spectrography, written by experts in the field. The uncertainties in the interpretation of results are discussed and the most modern techniques in the examination of very small samples are described.

Progress in Nuclear Energy Series IX, Analytical Chemistry, Volume 7: H. A. ELION and D. C. STEWART, Eds. Pergamon, Oxford, 1966. Pp.v +288. £4 10*s*.

This volume maintains the high standard of the series. The main emphasis is on instrumental methods particularly those connected with surface studies, with articles on electron diffraction (R. K. Hart), ion microprobe mass spectrometer (A. E. Barrington, R. F. K. Herzog and W. P. Poschenrieder) and a table of coefficients for microprobe analysis (R. D. Dewey), which is coupled with tables of X-ray data (R. D. Dewey, R. S. Mapes and T. W. Reynolds). A long, 90-page, article on liquid scintillator solutions (D. L. Horrocks) and a comprehensive review of in-line analytical instrumentation of nuclear fuel processing plants (C. R. McGowan and J. K. Foreman) complete the volume. Only a few references are to articles printed later than 1964.

Talanta, 1967, Vol. 14, p. ii. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Radiochemische Trennungen mit Hilfe der Ringofenmethode—I. Das system $^{137}Cs/^{137m}$ Ba: D. KLOCKOW (5 *August* 1966)

Elektronisches Rechnen in der Analytischen Chemie—II. Algo-Programm für die einfache Varianz-analyse: G. GOTTSCHALK (9 *September* 1966)

L'application des radioisotopes á la chromatographie sur colonnes de celluloses substituées—IV. L'analyse du mercure et du zinc dans le bismuth: R. A. A. MUZZARELLI and G. MARCOTRIGIANO (21 *October* 1966)

On the concentration and identification of trace elements in sea water—I: C. L. DORIAN and N. R. ANDERSEN (27 *October* 1966)

Amperometry with two polarizable electrodes—XIII. Chelometric determination of iron and aluminium: F. VYDRA and K. ŠTULÍK (27 *October* 1966)

Rapid solvent extraction and direct spectrophotometric determination of gold (III) with 2-thenoyltri-fluoroacetone: A. V. RANGNEKAR and S. M. KHOPKAR (28 *October* 1966)

Spectrophotometric investigation of ascorbic acid complexes of metals: K. P. STOLYAROV and I. A. AMANTOVA (28 *October* 1966)

The stability constants of TAR and PAR complexes: R. A. CHALMERS (2 *November* 1966)

Present state of complexometry—III. Determination of monovalent metals: R. PŘIBIL (3 *November* 1966)

Spectrophotometric determination of channel black in small arms propellants: M. GALAN and G. NORWITZ (3 *November* 1966)

Precipitation from homogeneous solution by photochemical action: M. DAS, A. H. A. HEYN and M. Z. HOFFMAN (3 *November* 1966)

Steric hindrance effects in the use of heterocyclic azodyestuffs as colorimetric reagents: W. J. GEARY and F. BOTTOMLEY (14 *November* 1966)

L'utilisation du titrage enthalpimétrique à la détermination de la chaleur de neutralisation de quelques amines secondaires et tertiaires: E. POPPER, L. ROMAN and P. MARCU (14 *November* 1966)

Sur la détermination des chaleurs de neutralisation de quelques amines aliphatiques par la méthode du titrage enthalpimétrique: E. POPPER, L. ROMAN and P. MARCU (14 *November* 1966)

Coloured chelates with robinetin: M. KATYAL, S. PRAKASH and R. P. SINGH (15 *November* 1966)

***p*-Amino acetophenone as a reagent for the colorimetric determination of cerium(IV):** G. SOMIDEVAMMA and M. S. SARMA (16 *November* 1966)

Étude de la formation des dodecatungstates à l'aide du chlorure de tetraphenylphosphonium: R. RIPAN and C. CALU (17 *November* 1966)

Utilisation du chlorure de tetraphenylphosphonium pour le dosage des dodecatungstates et des tungstates alcalins: R. RIPAN and C. CALU (17 *November* 1966)

ADDENDUM

The following information was omitted from the papers by C. Drăgulescu, S. Policec and T. Simonescu which appeared on pages 1451 and 1543 of volume 13.

(*Received* 4 *February* 1966. *Accepted* 12 *April* 1966)

Talanta, 1967, Vol. 14, p. ii. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Radiochemische Trennungen mit Hilfe der Ringofenmethode—I. Das system $^{137}Cs/^{137m}$ Ba: D. KLOCKOW (5 *August* 1966)

Elektronisches Rechnen in der Analytischen Chemie—II. Algo-Programm für die einfache Varianz-analyse: G. GOTTSCHALK (9 *September* 1966)

L'application des radioisotopes á la chromatographie sur colonnes de celluloses substituées—IV. L'analyse du mercure et du zinc dans le bismuth: R. A. A. MUZZARELLI and G. MARCOTRIGIANO (21 *October* 1966)

On the concentration and identification of trace elements in sea water—I: C. L. DORIAN and N. R. ANDERSEN (27 *October* 1966)

Amperometry with two polarizable electrodes—XIII. Chelometric determination of iron and aluminium: F. VYDRA and K. ŠTULÍK (27 *October* 1966)

Rapid solvent extraction and direct spectrophotometric determination of gold (III) with 2-thenoyltri-fluoroacetone: A. V. RANGNEKAR and S. M. KHOPKAR (28 *October* 1966)

Spectrophotometric investigation of ascorbic acid complexes of metals: K. P. STOLYAROV and I. A. AMANTOVA (28 *October* 1966)

The stability constants of TAR and PAR complexes: R. A. CHALMERS (2 *November* 1966)

Present state of complexometry—III. Determination of monovalent metals: R. PŘIBIL (3 *November* 1966)

Spectrophotometric determination of channel black in small arms propellants: M. GALAN and G. NORWITZ (3 *November* 1966)

Precipitation from homogeneous solution by photochemical action: M. DAS, A. H. A. HEYN and M. Z. HOFFMAN (3 *November* 1966)

Steric hindrance effects in the use of heterocyclic azodyestuffs as colorimetric reagents: W. J. GEARY and F. BOTTOMLEY (14 *November* 1966)

L'utilisation du titrage enthalpimétrique à la détermination de la chaleur de neutralisation de quelques amines secondaires et tertiaires: E. POPPER, L. ROMAN and P. MARCU (14 *November* 1966)

Sur la détermination des chaleurs de neutralisation de quelques amines aliphatiques par la méthode du titrage enthalpimétrique: E. POPPER, L. ROMAN and P. MARCU (14 *November* 1966)

Coloured chelates with robinetin: M. KATYAL, S. PRAKASH and R. P. SINGH (15 *November* 1966)

***p*-Amino acetophenone as a reagent for the colorimetric determination of cerium(IV):** G. SOMIDEVAMMA and M. S. SARMA (16 *November* 1966)

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Talanta, 1967, Vol. 14, pp. ii to iii. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Progress in the Science and Technology of the Rare Earths, Vol. 2: Ed. LE ROY EYRING. Pergamon, Oxford, 1966. Pp. 366. 105*s*.

This is a well produced volume exactly described by its title. For some of the articles "progress" refers to advances made since the writing of Vol. 1 in 1960. The length of the articles ranges from 12 to 108 pages. The subject matter includes, in decreasing order of length, uses (H. H. and R. M. Mandle, over 1300 references), mixed cation oxides (W. Low), chalcogenides and pnictides (E. F. Westrum, over 400 references), halides (R. E. Thoma), solid-state chemistry of pure oxides (G. Brauer), the molecular-field model of exchange coupling (J. H. van Vleck), metal complexes (D. I. Ryabchikov and E. K. Korchemnaya), and preparation of pure metals (A. H. Daane). Emphasis is placed on thermodynamic and magnetic properties. The personal style of the authors, retained by the editor, results in some of the articles being very readable.

Reinststoffprobleme: I—Reinststoffdarstellung, II—Reinststoffanalytik: Eds. J. BARTHEL, G. GÜNZLER and G. EHRLICH. Akademie-Verlag, Berlin, 1966. Pp. XII + 599; XI + 707. 55 DDM each.

These are the first two of the three volumes of the proceedings of the 2nd International Symposium "Reinststoffe in Wissenschaft und Technik" held in Dresden, 28 September–2 October 1965. Practically every aspect of the problems of producing and analysing high-purity and ultrahigh-purity materials is covered in these two volumes, and the papers presented at the symposium should prove highly stimulating to chemists in general as well as to workers active in this field. A very useful feature is the provision of summaries in English, German and Russian. The editors are to be congratulated on being able to get the work out so quickly; events move so rapidly that reports of symposia are often well out of date by the time they appear.

Organicheskii Analyz (in Russian): A. P. TERENT'EV. Izdat Moscow University, Moscow, 1966. Pp. 408. 2 Rb 51 Kop.

This book contains the collected works of the author in the field of identification of organic substances and of elemental and functional group analysis. The main topics covered are elemental analysis, the "wet-combustion" methods, functional group analysis, identification, gasometric methods, the analytical reactions of double bonds, sulphonic acids and the use of sulphur trioxide, use of diazo compounds in analysis, polarimetric analysis, organic reagents, and molecular weight determination. Special apparatus and experimental techniques are described. The book should be of general interest to analytical chemists engaged in research and control work, and also to organic chemists.

Analysis of Copper and its Alloys: W. T. ELWELL and I. R. SCHOLES. Pergamon, Oxford, 1967. Pp. xiii + 183. 50*s*.

This book gives a selection of methods, both chemical and instrumental, for the determination of 30 elements in copper and its alloys. The methods have all been tested and assessed in the authors' laboratories, and a particularly useful feature of the book is the quotation of the precision to be expected when these methods are used. The scope and limitations of the methods are also discussed, and reference is made to many of the other methods that are available but are not discussed in detail in the book.

Chromatographic Methods, 2nd Edition: R. STOCK and C. B. F. RICE. Chapman and Hall, London, 1967. Pp. viii + 256. 42*s*.

The second edition of this useful handbook contains an expanded section on the more recent thin-layer chromatographic technique, and additional material on gel-filtration. There are many useful table summarizing experimental details.

Polarographie: J. PROSZT, V. CIELESZKY and K. GYÖRBIRÓ. Akadémiai Kiadó, Budapest, 1967. Pp. 587. £7.

This book (written in German) is a useful compendium of polaragraphic methods. The theoretical section describes classical polarography and its modern developments, and is followed by sections on inorganic and organic applications of the polarographic method. These sections take the form of reviews of the literature, and there are working details given for selected inorganic methods.

A Generalized Outline of the Metabolism of Steroid Hormones: DINESH C. SHARMA and RALPH I. DORFMAN. Holden-Day, 500 Sansome St., San Francisco, 1966. $8.50.

A wall-chart showing the biosynthesis and catabolism of these hormones.

Chemie in unserer Zeit. Verlag Chemie GmbH, Weinheim. DM 18 per annum.

A new journal (written in German) of general chemical interest, appearing 6 times in the year. It is intended for the intelligent layman, schools, and scientists with a non-specialized interest in chemistry, and is produced under the auspices of the Gesellschaft Deutscher Chemiker.

Chemical Analysis of Radioactive Materials: A. K. LAVRUKHINA, T. V. MALYSHEVA and F. I. PAVLOTSKAYA. Iliffe, London, 1967. Pp. 10 + 386. 50*s*.

This translation from the Russian is divided into five sections dealing with behaviour of radioactive species in solution, the theory of radiochemical analysis, methods of identification of radioisotopes, isolation and concentration of radioactive species, and methods of obtaining radioactively pure species. There do not appear to be any references later than 1963, though the literature up to that date seems to be well covered.

Advances in Inorganic Chemistry and Radiochemistry, Vol. 9: H. J. EMÈLEUS and A. G. SHARPE, Editors. Academic Press, New York, 1966. Pp. xiii + 386. 124*s*.

This volume keeps up to standard of its predecessors and contains articles on liquid-liquid extraction of metal ions, nitrides of metals of the first transition series, pseudohalides of Group IIIB and IVB elements, stereoselectivity in coordination compounds, heterocations, and the inorganic chemistry of tungsten.

Talanta, 1967, Vol. 14, p. iii. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

POLAND

10–15 *September* 1968: **Third Polish Analytical Conference.** Organized by the Commission of Analytical Chemistry of the Polish Academy of Sciences under the auspices of the International Union of Pure and Applied Chemistry. To be held in Warsaw.

The main subjects to be dealt with are basic problems of analytical chemistry (new reagents, new reactions, ionic equilibria, accuracy and precision, etc.), analytical methods in inorganic and organic industry and technique of analytical chemistry (new apparatus, automation, standards, sampling, etc.). Abstracts of papers for the conference are required by 15 January 1968. Further details from: Dr Adam Hulanicki, Warszawa 22, ul. Pasteura 1, Poland.

U.S.A.

18–23 *August* 1968: **Second International Conference on Thermal Analysis,** Holy Cross College, Worcester, Massachusetts, U.S.A.

Further details from Dr. J. P. Redfern (U.K. ICTA Liaison Officer) Stanton Instruments Ltd., Copper Mill Lane, London, S.W.17 (Tel. 01-946 7731).

Talanta, 1967, Vol. 14, p. iii. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

The XXIst International Congress of Pure and Applied Chemistry will be held in Prague, 4–10 September 1967. Three topical subjects have been selected which will be dealt with in three sections:

Automation in Analytical Chemistry

Toxicological Chemistry

Chemistry of Nucleic Acid Components.

The Second Circular of the Congress, with full information, may be obtained on request from:

Organizing Committee XXIst International Congress of Pure and Applied Chemistry, P.O.B. 139, Praha 6-Dejvice, Czechoslovakia.

The time-limit for application for participants who intend to present a paper terminates on 1 March 1967 and for other participants on 31 May 1967.

GERMANY

The Analytical Chemistry Group of the German Chemical Society will hold a meeting on "Methods of Structure Analysis of Organic Compounds" in Berlin, 21–23 September 1967. Plenary lectures will be given on "Methods of Structure Analysis", "Structure Analysis by Mass Spectrometry", Optical Rotation and Circular Dichroism Applied to Conformational Analysis" and "Characterization of High Polymers". Intending contributors should send 5 copies of a 200-word abstract of their paper not later than 17 February 1967 to Geschäftsstelle der Gesellschaft Deutscher Chemiker, Herrn Dr. Fritsche, 6 Frankfurt/Main 9, Postfach 9075, from whom further particulars may be obtained.

The Group will also hold a meeting on "Analysis and Chemistry of Enamels" in Freudenstadt (Schwarzwald), 9–11 May 1967. Abstracts of papers (which may be in English, French or German) should be sent (5 copies, 200 words) not later than 15 February 1967 to Prof. Dr. W. BUES, Laboratorium für anorganische und analytische Chemie der Universität Tübingen, 74 Tübingen, Wilhelmstraße 33, from whom further details may be obtained.

UNITED KINGDOM

Solvent Extraction Group

This group has recently been formed (details from the Secretary, Mr. A. A. North, Warren Spring Laboratory, Gunnels Wood Road, Stevenage, Herts., U.K.) to foster interest in the technique of solvent extraction. Its immediate aims are to outline the existing state of knolwedge and demonstrate the possibilities of the technique, and to indicate some of the problems involved in its technical application. A half-day meeting on the theme "Principles of Industrial Solvent Extraction" will be held in four centres in different parts of the country in order to introduce the Group and its aims to as wide an audience as possible. The meetings will begin at 2.30 p.m. on the following dates:

23 January 1967, at 14 Belgrave Squate, London S.W.1.

15 February 1967, at the Houldsworth School of Applied Science, The University, Leeds.

1 March 1967, at the Technical College, Falkirk.

12 April 1967, at the University of Technology, Loughborough.

Papers will be given on "The Chemistry of Solvent Extraction", "Process Design" and "Industrial Contacting Equipment".

ERRATUM

G. GOPALA RAO: Potassium dichromate as an oxidimetric reagent, *Talanta*, 1966, **13**, 1473–1495.

On p. 1476 of the November issue and the 10th line under the heading "Species present at high acid concentration", the sentence beginning "The presence of . . ." should read:

The presence of $(CrSO_7^{2-})$,[14] (CrO_2^{+})[19] and $HOCrO_2(OSO_3H)$[17,20] in sulphuric acid solutions has been reported.

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Variamine Blue as a gravimetric reagent. Determination of tungsten: L. ERDEY, I. BUZÁS and K. VIGH, *Talanta*, 1967, **14**, 515 (Institute for General Chemistry, Technical University, Budapest XI, Hungary).

Summary—Tungsten can be precipitated by a solution of Variamine Blue at pH 5. The precipitate is ignited to constant weight at a temperature above 600° and weighed as tungsten trioxide. The method can be used for the determination of tungsten in alloy steels.

Radiometric determination of submicrogram amounts of mercury: JIŘÍ STARÝ and RADULE MILOŠEVIĆ, *Talanta*, 1967, **14**, 521 (Department of Nuclear Chemistry, Faculty of Technical and Nuclear Physics, Prague, Czechoslovakia).

Summary—A radiometric method for the determination of submicrogram amounts of mercury (down to 5×10^{-10} g/ml) is described. The method is based on the exchange reaction between mercury and silver–110m dithizonate. Only palladium, gold, silver, and large amounts of copper and bismuth interfere in the determination, and must be removed.

Extractive photometric determination of thorium with arsenazo DAL: BŘETISLAV BUDĚŠÍNSKÝ and BLANKA MENCLOVÁ, *Talanta*, 1967, **14**, 523 (Nuclear Research Institute, Czechoslovak Academy of Sciences, Řež near Prague, Czechoslovakia).

Summary—Arsenazo DAL, the dianilide of 3,6-bis(2′-arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulphonic acid, is proposed as an extractive photometric reagent for the highly selective determination of trace amounts of thorium.

The stability constants of TAR and PAR complexes: ROBERT A. CHALMERS, *Talanta*, 1967, **14**, 527 (Chemistry Department, University of Aberdeen, Old Aberdeen, Scotland).

Summary—A discussion is given of the problem of ascribing dissociation constants in the hypothetical situation in which the protons of the hydroxy groups of TAR and PAR dissociate in the reverse of the normal order, and it is suggested that the *o*-hydroxy group should be regarded as intrinsically as acidic as the *p*-hydroxy group, and that the change in p*K* due to the internal hydrogen bonding is probably less than one unit.

SUMMARIES FOR CARD INDEXES

Separation of tin from other elements by partition chromatography: JAMES S. FRITZ and GARY L. LATWESEN, *Talanta*, 1967, **14**, 529. (Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A.)

Summary—Tin(IV) is separated quantitatively from many other metal ions by reversed-phase chromatography on a column of solid support impregnated with an organic liquid. When aqueous 8*M* hydrochloric acid is used as the eluent, tin(IV) is retained on a column impregnated with methyl isobutyl ketone and is separated quantitatively from bismuth(III), cadmium(II), copper(II), lead(II), mercury(II) and zinc(II). For the separation of tin(IV) and molybdenum(VI) the aqueous eluting phase is 1*M* hydrochloric acid–3*M* sulphuric acid. A column impregnated with isopropyl ether quantitatively retains antimony(V) from 8*M* hydrochloric acid and permits tin(IV) to be eluted rapidly.

Steric hindrance effects in the use of heterocyclic azodyestuffs as spectrophotometric reagents: W. J. GEARY and F. BOTTOMLEY, *Talanta*, 1967, **14**, 537 (Department of Chemistry and Metallurgy, Lanchester College of Technology, Coventry, England).

Summary—The heterocyclic azo dyestuffs 4-(*n*-methyl-2′-pyridylazo)-resorcinol (where $n = 3'$, $4'$, $5'$, $6'$) have been prepared, and their possible use as spectrophotometric reagents investigated. The dyestuffs are shown to function analogously to the parent ligand 4-(2′-pyridylazo) resorcinol (PAR) in giving red complexes with the ions Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and UO_2^{2+}. Steric effects resulting from the position of the methyl group in the heterocyclic ring are shown to occur in relation both to the spectra of the dyestuffs themselves and to the sensitivity of their reactions with the metal ions.

Extraction of reduced molybdosilicic acid and its application to the determination of traces of silicon: YACHIYO KAKITA and HIDEHIRO GOTO, *Talanta*, 1967, **14**, 543 (Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai, Japan.)

Summary—It is difficult to find satisfactory organic solvents for the extraction of reduced molybdosilicic acid, but extraction is possible with isoamyl or isobutyl alcohol if the acid concentration of the aqueous solution is increased before the extraction, the best results being obtained by extraction with isoamyl alcohol from 3·5–4·5*N* sulphuric acid medium. This makes the reduced molybdosilicic acid method much more sensitive and permits the determination of microgram amounts of silicon in various kinds of high-purity metals.

ОТДЕЛЕНИЕ ОЛОВА ОТ ДРУГИХ ЭЛЕМЕНТОВ МЕТОДОМ РАСПРЕДЕЛИТЕЛЬНОЙ ХРОМАТОГРАФИИ:

JAMES S. FRITZ and GARY L. LATWESEN, *Talanta*, 1967, **14**, 529.

Резюме—Олово(IV) отделяется количественно от числа других ионов металлов методом хроматографии на обратной фазе, пользуясь колонкой наполненой твердым носителем, пропитанным органической жидкостью. В случае использования 8*M* соляной кислоты в качестве элюента, олово(IV) задерживается на колонке пропитанной метилизобутилкетоном и этим образом отделяется количественно от висмута(III), кадмия(II), меди(II), свинца(II), ртути(II) и цинка(II). Для разделения олова(IV) и молибдена(VI) пользуются смесью 1*M* соляной кислоты и 3*M* серной кислоты в качестве водяного элюента. Пропитанная изопропиловым эфиром колонка задерживает количественно сурьму(V) из раствора 8*M* соляной кислоты и позволяет быстрое элюирование олова(IV).

ВЛИЯНИЕ ПРОСТРАНСТВЕННОГО ЗАТРУДНЕНИЯ НА ИСПОЛЬЗОВАНИЕ ГЕТЕРОЦИКЛИЧЕСКИХ АЗОКРАСИТЕЛЕЙ В КАЧЕСТВЕ СПЕКТРОФОТОМЕТРИЧЕСКИХ РЕАГЕНТОВ:

W. J. GEARY and F. BOTTOMLEY, *Talanta*, 1967, **14**, 537.

Резюме—Приготовлены гетероциклические азокрасители типа 4-(н-метил-2 -пиридилазо)резорцина (где н = 3′, 4′, 5′, 6′) и изучена их применимость в качестве спектрофоторетрических реагентов. По аналогии с основным лигандом 4-(2 -пиридилазо)резорцином (ПАР) красители дают красные комплексы с ионами Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, и VO_2^{2+}. Вызванные положением метилгруппы в гетероциклическом кольце пространственные эффекты показывают их влияние на спектры самых красителей и на чувствительность их реакций с ионами металлов.

ИЗВЛЕЧЕНИЕ ВОССТАНОВЛЕННОЙ КРЕМНЕМОЛИБДЕНОВОЙ КИСЛОТЫ И ЕГО ИСПОЛЬЗОВАНИЕ ДЛЯ ОПРЕДЕЛЕНИЯ СЛЕДОВ КРЕМНИЯ:

YACHIYO KAKITA and HIDEHIRO GOTO, *Talanta*, 1967, **14**, 543.

Резюме—Трудно найти удовлетворительные органические растворители для извлечения восстановленной кремнемолибденовой кислоты, но извлечение можно провести изоамиловым или изобутиловым спиртами если повышается кислотность водяного раствора пред извлечением; самые лучшие результаты получаются экстрагированием изоамиловым спиртом из 3,5–4,5*N* сернокислой среды. Метод пользующийся восстановленной кремнемолибденовой кислоты гораздо больше чувствительний и позволяет определение микрограммовых количеств кремния в различных высокочистотных металлах.

Studies in atomic-fluorescence spectroscopy—III. Microwave-excited electrodeless discharge tubes as spectral sources for atomic-fluorescence and atomic-absorption spectroscopy: R. M. DAGNALL, K. C. THOMPSON and T. S. WEST, *Talanta*, 1967, **14**, 551 (Chemistry Department, Imperial College, London S.W.7, England.)

Summary—Details are given for the production and operation of microwave-excited electrodeless discharge tubes for use as sources in atomic-fluorescence and atomic-absorption spectroscopy. Special reference is made to the tubes for selenium and tellurium and their spectral characteristics are fully discussed. Optimum conditions are given for producing suitably intense and stable sources.

Studies in atomic-fluorescence spectroscopy—IV. The atomic-fluorescence spectroscopic determination of selenium and tellurium: R. M. DAGNALL, K. C. THOMPSON and T. S. WEST, *Talanta*, 1967, **14**, 557 (Chemistry Department, Imperial College, London S.W.7, England.)

Summary—Selenium and tellurium are determined down to 0·25 and 0·12 ppm respectively by measuring the atomic-fluorescence signals at 2040 Å and 2143 Å respectively. Other possible wavelengths of measurement are considered in detail and the effects of some extraneous ions are examined. Microwave-excited electrodeless discharge tubes are used as spectral sources and intensity measurements are made with a Unicam SP 900A atomic-absorption/flame-emission spectrophotometer. Atomic-absorption measurements are also made with the same sources and spectrophotometer. The advantages of atomic-fluorescence methods and the use of electrodeless discharge tubes are discussed.

Photon-activation analysis of caesium: C. PERSIANI, J. SPIRA and R. BASTIAN, *Talanta*, 1967, **14**, 565 (Republic Aviation Corp., Farmingdale, N.Y., U.S.A.)

Summary—The corrosive behaviour of caesium has been attributed in part to the presence of a non-metallic impurity such as oxygen. A photon-activation method for determining oxygen and carbon in caesium is described. Scintillation coincidence-counting and pulse-height discrimination are used to count the gamma-ray activity resulting from annihilation of the positrons emitted. Variation of beam energy has been investigated in order to obtain optimum irradiation conditions. In the samples analysed and under the conditions used, less than 100 ppm of oxygen and carbon can be detected. Results are compared with those from other methods.

ИЗУЧЕНИЕ АТОМНО-ФЛУОРЕСЦЕНТНОЙ СПЕКТРОСКОПИИ—III. ВОЗБУЖДЕННЫЕ МИКРОВОЛНАМИ БЕЗЭЛЕКТРОДНЫЕ РАЗРЯДНЫЕ ЛАМПЫ КАК СПЕКТРАЛЬНЫЕ ИСТОЧНИКИ ДЛЯ АТОМНО-ФЛУОРЕСЦЕНТНОЙ И АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОСКОПИИ:

R. M. Dagnall, K. C. Thompson and T. S. West, *Talanta*, 1967, **14**, 551.

Резюме—Приведены детали изготовления и использования возбужденных микроволнами безэлектродных разрядных ламп в качестве источников в атомно-флуоресцентной и атомно-абсорбционной спектроскопиях. Авторы особенно отсыляются к лампами для селена и теллура и обсуждают их спектральные характеристики. Приведены оптимальные условия для произведения интенсивных и устойчивых источников.

ИЗУЧЕНИЕ АТОМНО-ФЛУОРЕСЦЕНТНО Й СПЕКТРОСКОПИИ—IV. ОПРЕДЕЛЕНИЕ СЕЛЕНА И ТЕЛЛУРА МЕТОДОМ АТОМНО-ФЛУОРЕСЦЕНТНОЙ СПЕКТРОСКОПИИ:

R. M. Dagnall, K. C. Thompson and T. S. West, *Talanta*, 1967, **14**, 557.

Резюме—Селен и теллур определили все до 0,25 и 0,12 частей на миллион соответственно, измерением сигналей атомной флуоресценции при 2040 Å и 2143 Å соответственно. Детально обсуждены другие используемые длины волн и испытано влияние некоторых чуждых ионов. Возбужденные микроволнами безэлектродные разрядные лампы использовали в качестве спектральных источников а измерение интенсивности проводили на спектрофототометре Юникам SP 900A для атомной абсорбции и пламенной емиссии. Измерения атомной абсорбции проведены на том же самои спектрометре и пользуясь тем же самим источниками. Обсуждены преимущества методов атомной флуоресценции и безэлектродных разрядных ламп.

ФОТОННЫЙ АКТИВАЦИОННЫЙ АНАЛИЗ ЦЕЗИЯ:

C. Persiani, J. Spira and R. Bastian, *Talanta*, 1967, **14**, 565.

Резюме—Коррозионная характеристика цезия приписана частью присутствии неметаллических примесей, как на пример кислорода. Описан метод фотонноактивационного анализа для определения кислорода и углерода в цезии. Сцинтиллационный счетчик и анализатор импульсов использованы для измерения активности гамма лучей, образующихся в результате уничтожения вылетающих позитронов. Изучено влияние изменения энергии пучка с целью определения оптимальных условий облучения. В исследованных образцах и условиях опыта удалось обнаружить меньше чем 100 частей на миллион кислорода и углерода. Полученные этим методом результаты сравнены с результатами других методов.

Rapid microchemical method for the determination of magnesium in biological fluids: U. P. S. CHAUHAN and P. C. PANDE, *Talanta*, 1967, **14**, 575 (Institute of Nuclear Medicine and Allied Sciences, Delhi-7, India.)

Summary—A photometric method for the determination of magnesium in the presence of up to 50-fold excess of calcium is described. A magnesium–Azovan Blue lake is formed, stabilized with polyvinyl alcohol, and the absorbance is measured (Kodak No. 7 filter). The method has been used to determine magnesium in sera.

Applicability of the quasi-adiabatic enthalpimetric method for the study of chemical kinetics: PAOLO PAPOFF and PIER GIORGIO ZAMBONIN, *Talanta*, 1967, **14**, 581 (Istituto Chimica Analitica, Universita di Bari, Italy.)

Summary—The thermal quasi-adiabatic method and the non-adiabatic one are compared for the study of chemical kinetics. With thermistors as temperature-sensitive elements, and a very simple apparatus, moderately fast reactions (with $t_{1/2}$ down to 2 sec) and consecutive reactions can be followed, and mixtures analysed with good accuracy. The reproducibility is satisfactory over a wide range of experimental conditions. The calculation of the kinetic parameters, for both first- and second-order kinetics is very simple and requires no calibration of the system. Application of the technique to the study of the alkaline hydrolysis of some alkyl acetates is described.

1-Hydroxy-ethylidene-1,1-diphosphonic acid as a titrimetric agent: R. PŘIBIL and V. VESELÝ, *Talanta*, 1967, **14**, 591 (Laboratory for Analytical Chemistry, J. Heyrovský Polarographic Institute, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia.)

Summary—1-Hydroxy-ethylidene-1,1-diphosphonic acid (HEDPHA) has been proposed as a highly selective titrimetric reagent for thorium. In the presence of 1,2-diaminocyclohexanetetra-acetic acid (DCTA) a soluble binuclear ternary complex, $Th_2(DCTA)_2(HEDPHA)$, is formed. The determination of thorium is carried out in a slightly acidic medium, buffered with urotropine, with 0·025*M* HEDPHA, and Xylenol Orange as indicator. DCTA masks all bivalent metals, rare earths, scandium, yttrium, bismuth, iron, gallium and indium. Only zirconium, titanium, aluminium and large amounts of thallium(III) interfere.

БЫСТРЫЙ МИКРОХИМИЧЕСКИЙ МЕТОД ОПРЕДЕЛЕНИЯ МАГНИЯ В БИОЛОГИЧЕСКИХ ЖИДКОСТЯХ:

U. P. S. Chauhan and P. C. Pande, *Talanta*, 1967, **14**, 575.

Резюме—Описан фотометрический метод определения магния в присутствии 50 кратного избытка кальция. Образуется стабилизированный поливиниловым спиртом лак магния с азовансином, светопоглощение которого измеряют с использованием фильтра Кодак Но. 7. Метод применен в определении магния в сыворотке.

ПРИМЕНИМОСТЬ КВАЗИАДИАБАТИЧЕСКОГО ЭНТАЛЬПИМЕТРИЧЕСКОГО МЕТОДА ДЛЯ ИЗУЧЕНИЯ КИНЕТИКИ ХИМИЧЕСКИХ РЕАКЦИЙ:

Paolo Papoff and Pier Giorgio Zambonin, *Talanta*, 1967, **14**, 581.

Резюме—Сравнена применимость квазиадиабатического и неадиабатического методов для изучения кинетики химических реакций. Пользуясь термисторами в качестве элементов для обнаружения температуры и весьма простой аппаратурой, можно следить умеренно быстрые реакции (имеющие $t_{1/2}$ выше 2 сек.) и последующие реакции, и анализировать смеси с довольном точностью. Воспроизводимость результатов удовлетворительна в широких пределах опытных условий. Вычисление кинетических параметров для реакций первого и второго порядка весьма простое и не требует калибровку системы. Описано применение процедуры на изучение щелочного гидролиза некоторых алкилацетатов.

1-ОКСИЭТИЛИДЕН-1,1-ДИФОСФОНОВАЯ КИСЛОТА КАК ТИТРИМЕТРИЧЕСКИЙ АГЕНТ:

R. Přibil and V. Veselý, *Talanta*, 1967, **14**, 591.

Резюме—1-оксиэтилиден-1,1-дифосфоновая кислота(ОЭДФК) предложена в качестве высокоизбирательного титримет рического агента для тория. В присутствии 1,2-диаминоциклогексантетрауксусной кислоты (ДЦТА) образуется растворимый бинуклеарный третичный комплекс Th_2(ДЦТА)$_2$-логексантетрауксусной кислоты (ДЦТА) образуется раст-(ОЭДФК). Определение тория проводится в слабокислом, забуферированном уротропином растворе с 0,025*M* ОЭДФК и ксиленолоранжевым в качестве индикатора. ДЦТА маскирует все двувалентные металлы, редкоземельные элементы, скандий, иттрий, висмут, железо, галлий и индий. Только цирконий, титан, алюминий и большие количества таллия(III) мешают определению.

Determination of microgram quantities of tin(IV) by a combined ion-exchange/X-ray fluorescence technique: B. R. CHAMBERLAIN and R. J. LEECH, *Talanta*, 1967, **14**, 597. (Pilkington Brothers Limited, Research and Development Laboratory, Lathom, Ormskirk, Lancashire, U.K.)

Summary—A method is described for the analysis of microgram quantities of tin in dilute hydrofluoric acid. The tin is extracted onto anion-exchange resin loaded paper discs by a very simple technique and the papers are examined by X-ray fluorescence spectrography. The solutions are obtained by the dissolution of tin-containing glasses, and the normal glass-forming elements do not interfere. The method is intended for the determination of 1–20 μg of tin but may be used for up to at least 250 μg; 5 μg can be determined with a precision of $\pm 10\%$

Spectrophotometric determination of Channel Black in small arms propellants: MICHAEL GALAN and GEORGE NORWITZ; *Talanta*, 1967, **14**, 603 (Frankford Arsenal, Philadelphia, Pa., U.S.A.)

Summary—A spectrophotometric method is proposed for the determination of Channel Black in small arms propellants. The Channel Black is separated from the nitrocellulose and other organic compounds by dissolution of the propellant in morpholine and filtration through a sintered porcelain crucible containing an asbestos mat. The Channel Black is then dissolved by treating the mat and crucible with boiling nitric acid for 3 hr, the solution is filtered, and the yellow colour is measured. The colour is due to polycarboxylic acids with cyclic nuclei. The range of the method is from 0 to 0·5% of Channel Black.

Synthetic and analytical studies on colour reagents—IX. The reactions of phthaleinazo compounds with the alkaline earths: TOSHIKO KOBATAKE, TADASHI IWACHIDO and KYOJI TÔEI, *Talanta*, 1967, **14**, 607 (Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama-shi, Japan.)

Summary—Some new phthaleinazo compounds—*o,o'*-dihydroxyazo compounds—have been prepared by coupling chromotropic acid, R-acid, and 2-hydroxy-3-naphthoic acid with bis-diazotized diaminophthaleins. These compounds have been found to be very sensitive colour reagents for alkaline earths in alkaline media, and in particular, bis(chromotropeazo)phenolphthalein is the most sensitive yet found.

New method for the determination of pentachlorophenol by atomic absorption spectrophotometry: Y. YAMAMOTO, T. KUMAMARU and Y. HAYASHI, *Talanta*, 1967, **14**, 611 (Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima, Japan.)

Summary—A new application of atomic absorption is reported for the determination of pentachlorophenol. The method is based on solvent extraction into nitrobenzene of the ion-pair formed between tris(1,10-phenanthroline)iron(II) and the anion of pentachlorophenol, and the subsequent determination of the iron concentration in the extract by atomic absorption at the 2483 Å iron line.

ОПРЕДЕЛЕНИЕ МИКРОГРАММОВЫХ КОЛИЧЕСТВ ОЛОВА(IV) КОМБИНИРОВАННОЙ ПРОЦЕДУРОЙ ИОННОГО ОБМЕНА И ФЛУОРЕСЦЕНЦИИ РЕНТГЕНОВСКИХ ЛУЧЕЙ:

B. R. Chamberlain and R. J. Leech, *Talanta*, 1967, **14**, 597.

Резюме—Описан метод анализа микрограммовых количеств олова в разбавленной фтористоводородной кислоте. Олово концентрируют на пропытанных анионообменной смолой бумажных дисках, следуя весьма простую процедуру и диски испытывают методом флуоресценции рентгеновских лучей. Растворы получены растворением оловосодержающих стекл, а обыкновенные стеклообразующие элементы не мешают определению. Метод разработан для определения 1–20 мкг олова, нотможет применяться все до 250 мкг и выше; точность определения 5 мкг равна ±10%.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ КАНАЛЬНОЙ САЖИ В РЕАКТИВНЫХ ТОПЛИВАХ ДЛЯ МАЛЫХ ОРУЖИЯХ:

Michael Galan and George Norwitz, *Talanta*, 1967, **14**, 603.

Резюме—Предложен спектрофотометрический метод определения канальной сажи в топливах для малых оружиях. Канальную саж отделяют от нитроцеллюлозы и других органических веществ растворением топлива в морфолине и фильтрованием через спеченный фарфоровый тигель с вставкой из асбестовой ткани. Канальную сажу затем растворяют помещением асбестовой ткани и тигеля в кипящую азотную кислоту и обрабативанием в течение 3 часа; раствор фильтруют и измеряют его желтый цвет. Цвет вызван поликарбоновыми кислотами с циклическими ядрами. Метод применимый в пределах 0 до 0,5% канальной сажи.

СИНТЕТИЧЕСКОЕ И АНАЛИТЧЕСКОЕ ИЗУЧЕНИЕ ОКРАШИВАЮЩИХ РЕАГЕНТОВ—IX. РЕАКЦИИ ФТАЛЕИНАЗОСОЕДИНЕНИЙ С ЩЕЛОЧНОЗЕМЕЛЬНЫМИ ЭЛЕМЕНТАМИ:

Toshiko Kobatake, Tadashi Iwachido and Kyoji Tôei, *Talanta*, 1967, **14**, 607.

Резюме—Некоторые новые фталеиназосоединения—*o,o'*-диоксиазосоединения—приготовлены путем сочетания хромотроповой, Р—кислоты и 2-окси-3-нафтойной кислоты с бисдиазотированными диаминофталеинами. Эти соединения являются очень чувствительными окрашивающими реагентами для щелочноземельных элементов в щелочной среде; бис(хромотропазо)фенолфталени является наиболее чувствительным реагентом найденым до сих пор.

НОВЫЙ МЕТОД ОПРЕДЕЛЕНИЯ ПЕНТАХЛОРОФЕНОЛА МЕТОДОМ АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОФОТОМЕТРИИ:

Y. Yamamoto, T. Kumamaru and Y. Hayashi, *Talanta*, 1967, **14**, 611.

Резюме—Сообщено применение метода атомно-абсорбционной спектрофотометрии для определения пентахлорофенола. Метод основывается на извлечении нитробензолом ионной пары образующейся между трис(1,10-фенантролин) железом(II) и анионом пентахлорофенола, с последовательным определением концентрации железа в екстракте методом атомно-абсорбционной спектрофотометрии, пользуясь линией железа при 2483 Å.

SUMMARIES FOR CARD INDEXES

A critical review of methods of isolating and separating the noble metals—II: Ion-exchange and solvent extraction: F. E. BEAMISH, *Talanta*, 1967, **14**, 991 (Department of Chemistry, University of Toronto, Toronto 5, Ontario, Canada.)

Summary—This review deals with ion-exchange and solvent extraction methods of separating the seven noble metals, published subsequent to the previous reviews and prior to January 1966. The noble metal species present in solution are discussed in so far as they relate to separation and determination.

Spectroscopy in separated flames—I. The use of the separated air–acetylene flame in thermal emission spectroscopy: G. F. KIRKBRIGHT, A. SEMB and T. S. WEST, *Talanta*, 1967, **14**, 1011 (Chemistry Department, Imperial College, London, S.W.7.)

Summary—The separation of a premixed air–acetylene flame is described. The interconal zone of this flame exhibits very low radiative background, and is only slightly cooler than that of a normal air–acetylene flame. The use of the separated flame in flame photometry, for which it has several pronounced advantages, has been investigated.

Precipitation of nickel dimethylglyoximate: S. J. LYLE and R. MAGHZIAN, *Talanta*, 1967, **14**, 1021 (The Chemical Laboratory, The University of Kent at Canterbury, Canterbury, Kent, U.K.)

Summary—The homogeneous precipitation method of Salesin and Gordon and the aqueous acetone precipitation described by Jones and Howick are examined for the determination of nickel as the dimethylglyoximate and where applicable comparisons are made with a direct (conventional) precipitation of this substance. The co-precipitation of iron and cobalt was studied radiometrically under various experimental conditions. Relevant solubility data are also presented. Application of the methods to the determination of nickel in alloy steels showed that in the absence of cobalt there is little to choose between them. For cobalt steels the method of Jones and Howick is more convenient than that of Salesin and Gordon and more satisfactory than a conventional precipitation and gravimetric finish.

КРИТИЧЕСКИЙ ОБЗОР МЕТОДОВ ВЫДЕЛЕНИЯ РАЗДЕЛЕНИЯ БЛАГОРОДНЫХ МЕТАЛЛОВ—II: ИОННЫЙ ОБМЕН И ЭКСТРАКЦИЯ РАСТВОРИТЕЛЯМИ:

F. E. Beamish, *Talanta*, 1967, **14**, 991.

Резюме—Приведен обзор методов ионного обмена и экстракции растворителями для разделения семи благородных металлов, опубликованных после предыдущих обзоров, а раньше января 1966. Обсуждены только те ионы благородных металлов в растворе, относящиеся на разделение и определение этих металлов.

СПЕКТРОСКОПИЯ В РАЗДЕЛЕННОМ ПЛАМЕНИ—I. ИСПОЛЬЗОВАНИЕ РАЗДЕЛЕННОЙ ПЛАМЕНИ ВОЗДУХ-АЦЕТИЛЕН В ТЕРМИЧЕСКОЙ ЭМИССИОННОЙ СПЕКТРОСКОПИИ:

G. F. Kirkbright, A. Semb and T. S. West, *Talanta*, 1967, **14**, 1011.

Резюме—Описано разделение пламени из заранее смешанной смеси воздуха и ацетилена. Межконусная зона этой пламени имеет весьма низкий излучáющий фон и она только незначительно холоднее чем зона в обыкновенной пламени воздуха и ацетилена. Изучено применение раделенной пламени в пламенной фотометрии, для которого метода это пламя имеет некоторые преимущества.

ОСАЖДЕНИЕ ДИМЕТИЛГЛИОКСИМАТА НИКЕЛЯ:

S. J. Lyle and R. Maghzian, *Talanta*, 1967, **14**, 1021.

Резюме—Метод гомогенного осаждения Салесина и Гордона и метод осаждения водным раствором ацетона Джонса и Гауика применены в определении никеля в форме диметилглиоксимата и сравнены в некоторых случаях с прямым обыкновенным осаждением этого вещества. Соосаждение железа и кобальта изучено радиометрическим методом в различных опытных условиях. Приведены относящиеся к этим условиям данные о растворимости. Применение методов в определении никеля в легированных сталях показало хорошую применимость обоих методов в отсутсвии кобальта. В случае кобальтовых сталях более пригодным является метод Джонса и Гауика чем метод Салесина и Гордона, и более пригодным чем обыкновенное осаждение с весовым определением никеля.

A high speed micro vacuum-fusion apparatus: M. T. LILBURNE, *Talanta* 1967, **14**, 1029 (National Physical Laboratory, Teddington, Middlesex, England).

Summary—A micro vacuum-fusion apparatus capable of extracting, collecting and examining volumes of gas of no more than 2×10^{-3} cm^3 at N.T.P. from metal samples is described. The resulting gas mixture is analysed by gas chromatography with helium as the carrier gas and with a highly sensitive ionization detector.

Mass spectrometric analysis of high-purity helium and hydrogen, using a dynamic sampling and calibration system: R. T. PARKINSON, *Talanta*, 1967, **14**, 1037 (Master General of Ordnance Inspectorates, Chemical Inspectorate, Royal Arsenal, Woolwich, London S.E. 18, U.K.)

Summary—A dynamic gas sampling system has been designed for use with a mass spectrometer (A.E.I. Model MS2G). It is capable of sampling directly from gas streams at pressures in the region of 800 torr and has been satisfactorily used for the analysis of high-purity helium and hydrogen containing less than 50 vpm total impurity. The overall sensitivity is 1 vpm or better. The design permits the mass spectrometer to be used with its normal gas sampling system when required. A dynamic gas blending rig, incorporating a recirculation and purification system, has been developed for the calibration of the mass spectrometer over the range 5–100 vpm of impurity content.

Radioactive substoichiometric isotope-dilution procedure for the determination of rare earth metals: G. B. BRISCOE and A. DODSON, *Talanta*, 1967, **14**, 1051 (Department of Chemistry, University of Aston in Birmingham, Birmingham 4, England.)

Summary—A theory is developed which describes the equilibrium conditions when solutions containing trace metals and substoichiometric amounts of EDTA are extracted with thenoyltrifluoroacetone. Experimental evidence is given to support the theory. A method for the determination of microgram quantities of rare earth metal is outlined as an application.

ПРИБОР ДЛЯ ПЛАВЛЕНИЯ В ВАКУУМЕ НА МИКРОШКАЛЕ:

M. T. Lilburne, *Talanta*, 1967, **14**, 1029.

Резюме—Описан прибор для плавления в вакууме образцов металлов, которым можно экстрагировать, собирать и анализировать объемы газов меньше чем 2×10^{-3} см³ при нормальной температуре и давлении. Экстрагированная смесь газов анализируется методом газовой хроматографии, пользуясь гелием в качестве газа носителя и высокочувствительным ионизационным детектором.

АНАЛИЗ ВЫСОКОЧИСТОТНОГО ГЕЛИЯ И ВОДОРОДА МЕТОДОМ МАССПЕКТРОМЕТРИИ С ИСПОЛЬЗОВАНИЕМ ДИНАМИЧЕСКОЙ СИСТЕМЫ ДЛЯ ОТБОРА ПРОБЫ И КАЛИБРОВКИ:

R. T. Parkinson, *Talanta*, 1967, **14**, 1037.

Резюме—Сконструирована динамическая система отбора пробы газа для масс-спектрометра A.E.I. типа MS2G. Этой системой удается отобрать пробы прямо из струи газа при давлении в пределе 800 торр; ей пользовались успешно в анализе высокочистотного гелия и водорода, содержащего меньше чем 50 частей на миллион (по объему) общих примесей. Общая чувствительность метода больше чем I часть на миллион (по объему). Конструкция этой системы позволяет использование масс-спектрометра с его нормальной системой отбора газовидных проб в случае желания этого. Также сконструирована система для динамического смешивания газов, включая систему рециркуляции и очистки, которой пользовались для калибровки масс-спектрометра в пределах 5–100 частей на миллион (по объему) примеси.

СУБСТЕХИОМЕТРИЧЕСКАЯ ПРОЦЕДУРА РАЗБАВЛЕНИЯ РАДИОАКТИВНЫХ ИЗОТОПОВ ДЛЯ ОПРЕДЕЛЕНИЯ РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ:

G. B. Briscoe and A. Dodson, *Talanta*, 1967, **14**, 1051.

Резюме—Разработана теория описывающая равновесные условия при экстрагировании теноилтрифторацетоном растворов, содержащих следы металлов и субстехиометрические количества ЭДТА. Приведены экспериментальные данные подкрепляющие теорию. Методом пользовались для определения микрограммовых количеств редкоземельных металлов.

Purity control of uranium by neutron activation assay—II. Determination of manganese, nickel and copper: A. A. ABDEL-RASSOUL and S. S. WAHBA, *Talanta*, 1967, **14**, 1061 (Nuclear Chemistry Department, Atomic Energy Establishment, Cairo, U.A.R.)

Summary—Activation analysis is applied for the simultaneous determination of manganese, nickel and copper in different uranium samples, including metallic uranium, uranium concentrates, oxide, acetate, nitrate and sodium uranate. The analytical scheme developed is based on separation of the uranium by paper chromatography and subsequent determination of these elements in the pile-irradiated residues by simple radiochemical operations. The reliability of the scheme proposed is tested, and the limits of sensitivity of the methods worked out are ascertained. Accordingly, microgram concentrations of the elements studied could be assayed in limited quantities of the samples analysed with a precision of $\pm 15\%$. Reagent-blank determinations are also considered.

Cation-exchange behaviour of several elements in nitric acid–organic solvent media: J. KORKISCH, F. FEIK and S. S. AHLUWALIA, *Talanta*, 1967, **14**, 1069 (Analytical Institute, University of Vienna IX, Währingerstrasse 38, Austria.)

Summary—The cation-exchange behaviour of 19 elements towards the strongly acidic cation-exchange resin Dowex 50-X8 in media containing varying concentrations of organic solvents and aqueous nitric acid is reported. Based on the determination of the distribution coefficients of these elements in the organic solvents methanol, ethanol, n-propanol, isopropanol, methyl glycol, acetone, tetrahydrofuran and acetic acid, the conditions most suitable for their quantitative separation are indicated and discussed.

Titrimetric, coulometric and spectrophotometric determination of manganese following perchloric acid oxidation in the presence of pyrophosphate: JOHN KNOECK and HARVEY DIEHL, *Talanta*, 1967, **14**, 1083 (Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A.)

Summary—Manganese is oxidized quantitatively to a violet, tervalent pyrophosphate in a boiling mixture of equal parts of perchloric acid and phosphoric acid. This Mn(III) can be titrated potentiometrically or coulometrically with iron(II); it can also be measured spectrophotometrically. If the titrimetric method is carried out with titanium (III) or chromium(II), iron can also be titrated immediately after the manganese. The methods were applied to a new reference sample, ISU 600 Manganiferous Iron Ore, and to manganese ore, spiegeleisen, ferromanganese, and rail steel. Manganese(II) oxalate dihydrate has been reinvestigated as a primary standard and is highly recommended.

КОНТРОЛЬ ЧИСТОТЫ УРАНА МЕТОДОМ НЕЙТРОННО-АКТИВАЦИОННОГО АНАЛИЗА—II. ОПРЕДЕЛЕНИЕ МАРГАНЦА, НИКЕЛЯ И МЕДИ:

A. A. Abdel-Rassoul and S. S. Wahba, *Talanta*, 1967, **14**, 1061.

Резюме—Методом радиоактивационного анализа пользовались для одновременного определения марганца, никеля и меди в различных урансодержащих пробах, на пример в металлическом уране, концентратах урана, в окиси, ацетате, нитрате и в уранате натрия. Метод основывается на отделении урана методом бумажной хроматографии и последующем определении этих элементов в облученных в реакторе остатках применяя несложные радиохимические процедуры. Испытана надёжность предложенной схемы и определены пределы чувствительности методов. Этим образом удалось определить микрограммовые количества исследованных элементов точностью ±15% в ограниченных количествах анализируемых проб. Проведены также контрольные опыты для реагентов.

ИОНООБМЕННОЕ ПОВЕДЕНИЕ НЕКОТОРЫХ ЭЛЕМЕНТОВ В РАСТВОРАХ АЗОТНОЙ КИСЛОТЫ И ОРГАНИЧЕСКИХ РАСТВОРИТЕЛЯХ:

J. Korkisch, F. Feik and S. S. Ahluwalia, *Talanta*, 1967, **14**, 1069.

Резюме—Изучено катионообменное поведение 19 элементов на сильнокислой катионообменной смоле Дауекс 50-X8 в растворах, состоящихся из различных концентраций органических растворителей и водного раствора азотной кислоты. На основе коэффициентов распределения этих элементов в метиловом, этиловом, н-пропиловом и изопропиловом спиртах, метилгликоле, ацетоне, тетрагидрофуране и уксусной кислоте определены и обсуждены оптимальные условия для количественного выделения этих элементов.

ТИТРИМЕТРИЧЕСКОЕ, КУЛОНОМЕТРИЧЕСКОЕ И СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МАРГАНЦА ПОСЛЕ ОКИСЛЕНИЯ ХЛОРНОЙ КИСЛОТОЙ В ПРИСУТСТВИИ ПИРОФОСФАТА:

John Knoeck and Harvey Diehl, *Talanta*, 1967, **14**, 1083.

Резюме—Марганец окисляется количественно до фиолетового трехвалентного пирофосфата в кипящей смеси, состоящейся из равных частей хлорной и фосфорной кислот. Mn(III) можно титровать потенциометрическим или кулонометрическим методом с железом(II) или определять спектрофотометрическим методом. Если титрование проводится с титаном(III) или хромом(II), дана возможность титрования железа непосредственно после марганца. Метод использован в анализе нового эталона—ISU 600, содержащей марганец руды железа—и в анализе руды марганца, зеркального чугуна, ферромарганца и рельсовой стали. Снова изучено и рекомендовано использование дигидрата оксалата марганца (II) в качестве первичного стандарта.

Eléments de fluorimétrie organique fonctionnelle: M. PESEZ and J. BARTOS, *Talanta*, 1967, **14**, 1097 (Centre de Recherches Roussel-Uclaf, 93-Romainville, France.)

Summary—By means of suitable chemical reactions, formaldehyde is obtained from 1,2-diols, hexitols, primary α-amino alcohols, 2-nitro-1-hydroxy aliphatic compounds, the methylene group in R—CH=CH_2 and 17-ketolsteroids, and converted into a dihydrolutidine derivative which is then determined by fluorimetry. The formation of dihydropyridine derivatives also allows the fluorimetric determination of primary alkylamines, nitriles and aliphatic aldehydes. Aldehydes with an α-methylene group and 2-deoxysugars can be determined by forming fluorescent quinaldines. The fluorescent compound obtained by condensing glyoxylic acid with resorcinol allows the determination of α,β-dihydroxy and hexuronic acids after a periodate oxidation. The fluorimetric determination of phenols is achieved by converting them into coumarins.

Neutron activation analysis by standard addition and solvent extraction. Determination of impurities in aluminium: A. ALIAN and A. HAGGAG, *Talanta*, 1967, **14**, 1109 (Nuclear Chemistry Department, Atomic Energy Establishment, Inshas, U.A.R.)

Summary—A separation scheme based on the selective extraction in conjunction with the standard addition technique has been developed for the determination of impurities in aluminium by neutron activation. Preliminary investigations have been carried out on the extractability of Sc, Co, Hf, Fe, Sn, Cd, Zn, Ag, Cr, Ce, Cs and Rb by TDA and TBP from acidic media. The best conditions are predicted for the separation of these elements into fractions suitable for analysis by gamma-ray spectrometry. Recovery values of ~90% were obtained for all the elements.

Photometrische Bestimmung von Kupfer mit Polyäthylenimin: MAX ZIEGLER and LÜDER ZIEGELER, *Talanta*, 1967, **14**, 1121 (Anorganisch-Chemischen Institut, Die Universität, Göttingen, Deutschland.)

Summary—Copper (0·3–10%) in light metal alloys can be determined spectrophotometrically at 635 mμ by means of the colour produced with polyethylene imines. The reactions of these reagents with HNO_2, CS_2, HgI_2 and As_2O_3 have also been investigated.

ОСНОВЫ ФЛУОРОМЕТРИИ ОРГАНИЧЕСКИХ ФУНКЦИОНАЛЬНЫХ ГРУПП:

M. Pesez and J. Bartos, *Talanta*, 1967, **14**, 1097.

Резюме—Подходящими химическими реакциями можно получать формальдегид из 1,2-диолов, гекситолов, первичных α-аминоспиртов, 2-нитро-1-оксиалифатических соединений, метиленовой группы R—CH=CH_2 и 17-кетостероидов, и превращать его в дериват дигидролутидина, который затем определяют флуорометрическим методом. Образование дериватов дигидропиридина позволяет флуорометрическое определение первичных алкиламинов, нитрилов и алифатических альдегидов. Содержащие α-метиленовую группу альдегиды и 2-дезоксисахары можно определять путем образования флуоресцирующих хиналдинов. Флуоресцирующее соединение, полученное конденсацией глиоксалевой кислоты с резорцином позволяет определение α,β-диоксикислот и гексуроновых кислот после окисления периодатом. Флуорометрическое определение фенолов можно после их превращения в кумарины.

НЕЙТРОННОАКТИВАЦИОННЫЙ АНАЛИЗ ПУТЕМ ДОБАВЛЕНИЯ СТАНДАРТОВ И ЭКСТРАГИРОВАНИЯ РАСТВОРИТЕЛЯМИ. ОПРЕДЕЛЕНИЕ ПРИМЕСЕЙ В АЛЮМИНИИ:

A. Alian and A. Haggag. *Talanta*, 1967, **14**, 1109.

Резюме—Разработана основывающаяся на селективном извлечении схема разделения в связи с методом добавления стандартов для определения примесей в алюминии методом нейтронной активации. Проведены предварительные исследования экстрагируемости Sc, Co, Hf, Fe, Sn, Cd, Zn, Ag, Cr, Ce, Cs, и Rb из кислих растворов при помощи ТДА и ТБФ. Предсказаны оптимальные условия разделения этих элементов в фракции, анализируемые методом спектрометрии гамма лучей. Выход ~90% получен для всех этих элементов.

ФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МЕДИ ПОЛИЭТИЛЕНИМИНОМ:

Max Ziegler and Lüder Ziegeler, *Talanta*, 1967, **14**, 1121.

Резюме—Медь (0,3–10%) в сплавах лёгких металлов определяли спектрофотометрическим методом при 645 ммк, на основе окраски образованной с полиэтилениминами. Также изучены реакции этих реагентов с HIO_3, CS_2, HgI_2 и As_2O_3.

Synthesis and analytical applications of 2,4-dinitro-6-chlorophenylazothymol: S. K. MUKERJI and H. L. SHARMA, *Talanta*, 1967, **14**, 1123 (Geological Survey of India, Rajasthan Circle, Jaipur, India and Department of Pharmacology, S.M.S. Medical College, Jaipur, India.)

Summary—The newly synthesized 2,4-dinitro-6-chlorophenylazothymol, a weak acid with pK_a 8·33 ± 0·04 at 27°, is proposed as a sensitive spot reagent for magnesium, with an identification limit of 0·14 μg at pH 10·5–11·6. Silver and manganese(II) interfere but can be masked by means of cyanide and periodate respectively. There is little interference by anions. The reagent also serves as an acid–base indicator with a transition interval of pH 7–9, giving a sharp colour change at the equivalence point.

Studies on metallochromic indicators—I. Pyrocatecholphthalein as metallochromic indicator: G. K. SINGHAL and K. N. TANDON, *Talanta*, 1967, **14**, 1127 (Chemistry Department, Rajasthan University, Jaipur, India.)

Summary—Pyrocatecholphthalein has been used as a metallochromic indicator for the direct complexometric titrations of a number of metal ions with EDTA, both in acidic and in alkaline medium. Th, Bi(III), Ba, Sr, Ca, Mg, Mn(II), Pb(II), Cu(II), Cd, Ni, Co(II) and Zn have been successfully titrated. In comparison with Pyrocatechol Violet, this dyestuff gives sharper end-points when the titrations are done at high pH.

Interference of the ammonium ion in Mohr's method for the determination of chloride: JACOB BLOCK and OSCAR B. WATERS, JR., *Talanta*, 1967, **14**, 1130 (W. R. Grace and Co., Washington Research Center, Clarksville, Maryland 29029, U.S.A.)

Summary—The ammonium ion has been found to interfere in the Mohr method for the determination of chloride.

СИНТЕЗ И ПРИМЕНЕНИЕ В АНАЛИЗЕ 2,3-ДИНИТРО-6-ХЛОРОФЕНИЛАЗОТИМОЛА:

S. K. Mukerji and H. L. Sharma, *Talanta*, 1967, **14**, 1123.

Резюме—Недавно синтезированный 2,4-динитро-6-хлорофенилазотимол,—слабая кислота с pK_a 8,33 ± 0,04 при 27°—предложен в качестве чувствительного капельного реагента для магния, имеющий предел чувствительности 0,14 мкг при pH 10,5–11,6. Серебро и марганец(II) мешают, но их можно маскировать цианидом или периодатом, соответсвенно. Анионы почти не влияют на определение. Реагентом также можно пользоваться в качестве кислотно-щелочного индикатора, имеющим область перехода от pH 7–9, а дающим острую перемену цвета в точке еквиленватности.

ИЗУЧЕНИЕ МЕТАЛЛОХРОМНЫХ ИНДИКАТОРОВ—I. ПИРОКАТЕХИНФТАЛЕНИ В КАЧЕСТВЕ МЕТАЛЛОХРОМНОГО ИНДИКАТОРА:

G. K. Singhal and K. N. Tandon, *Talanta*, 1967, **14**, 1127.

Резюме—Пирокатехинфталеин использован в качестве металлохромного индикатора для прямого комплексонометрического титрования ряда ионов металлов с ЭДТА, в кислой и щелочной средах. Успешно титрованы Th, Bi(III), Ba, Sr, Ca, Mg, Mn(II), Pb(II), Cu(II), Cd, Ni, Co(II) и Zn. В сравнении с пирокатехинфиолетовым, этот краситель дает более острые конци титрования при высоких pH.

ВЛИЯНИЕ ИОНА АММОНИЯ НА ОПРЕДЕЛЕНИЕ ХЛОРИДА МАТОДОМ МОРА:

Jacob Block and Oscar B. Waters, Jr., *Talanta*, 1967, **14**, 1130.

Резюме—Установлено влияние иона аммония на определение хлорида методом Мора.

Substoichiometric determination of traces of gold by radioactive isotope-dilution analysis: D. A. BEARDSLEY, G. B. BRISCOE, J. RŮŽIČKA and M. WILLIAMS, *Talanta*, 1967, **14**, 879 (Department of Chemistry, The University of Aston in Birmingham, Birmingham 4, England).

Summary—A radioactive isotope-dilution method for the determination of traces of gold has been developed. It is based on the solvent extraction of gold diethyldithiocarbamate from 0·5*N* sulphuric acid containing ascorbic acid, by means of a substoichiometric amount of zinc diethyldithiocarbamate in chloroform. The separation has been applied to the analysis of gold-doped semiconductor-grade silicon and of gold-bearing ores. Amounts of gold down to 5×10^{-7} g/20 ml of test solution can be determined.

Study of the formation of dodecatungstates and the dosage of iso- and heterododecatungstates with the aid of chloride of tetraphenylphosphonium: RALUCA RIPAN and CLEOPATRA CALU, *Talanta*, 1967, **14**, 887 (Institut de chimie de l'Académie de la République Socialiste, Filiala Cluj Roumaine).

Summary—A physico-chemical study of the conditions of formation (pH, time, temperature) of dodecatungstates and of their separation with tetraphenylphosphonium chloride is presented. In the iso- and heteropolytungstate series only the anions of the form $XW_{12}O_{40}^{(8-n)-}$ (where n is the oxidation number of X) are precipitated by this reagent. The reaction is quantitative and can be used to separate the dodecatungstate from a mixture of tungstate anions. By using tetraphenylphosphonium chloride as a specific reagent for dodecatungstate it has been possible to show that in the condensation of sodium tungstate in high concentrations of acid the dodecatungstate begins to appear at pH $\sim$ 6 and all the tungstate is in this form at pH $\sim$ 2. Factors such as dilution, time and temperature also affect the formation of dodecatungstate over this pH range. The reaction is used for the determination of a series of dodecatungstates.

Reactions of Eriochrome Blue Black R: G. L. SILVER and R. C. BOWMAN, *Talanta*, 1967, **14**, 893 (Monsanto Research Corporation, Mound Laboratory, Miamisburg, Ohio, U.S.A.).

Summary—The reactions of Eriochrome Blue Black R with approximately 25 metals are tabulated. Photometric titrations of molybdenum and uranium are described, and a new method of titrating thulium with EDTA is presented.

Application of volatilazation-excitation curves to the determination of the conditions for spectrochemical analysis of tantalum oxide: J. BRIL and J. VINOT, *Talanta*, 1967, **14**, 897 (Cie Pechiney LRM-38- Grenoble, France).

Summary—The determination of the optimum conditions for the spectrographic analysis of tantalum oxide is facilitated by consideration of the volatilization curves for the elements sought. The method is applied for the estimation of Cr, Fe, Hf, Ni, Nb, Ti, Y and Zr at the 10–1000 ppm level.

СУБСТЕХИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ СЛЕДОВ ЗОЛОТА МЕТОДОМ РАЗБАВЛЕНИЯ РАДИОАКТИВНЫХ ИЗОТОПОВ:

D. A. Beardsley, G. B. Briscoe, J. Růžička and M. Williams, *Talanta*, 1967, **14**, 879.

Резюме—Разработан метод определения следов золота разбавлением радиоактивных изотопов. Метод основывается на экстрагировании диэтилдитиокарбамината золота субстехиометрическим количеством диэтилдитиокарбамината цинка в хлороформе из содержхющей аскорбиновую кислоту 0,5 *N* серной кислоты. Метод выделения был применен в анализе зараженного золотом кремния для полупроводников и руд золота. Метод позволяет определить до 5×10^{-7} г золота/20 мл анализируемого раствора.

ИЗУЧЕНИЕ ОБРАЗОВАНИЯ ДОДЕКАВОЛЬФРАМАТОВ И ОПРЕДЕЛЕНИЕ ИЗО- И ГЕТЕРОПОЛИВОЛЬФРАМАТОВ ХЛОРИДОМ ТЕТРАФЕНИЛФОСФОНИЯ:

Raluca Ripan and Cleopatra Calu, *Talanta*, 1967, **14**, 887.

Резюме—Сообщены результаты физико-химического изучения условий (pH, времени, температуры) образования додекавельфраматов и их разделения хлоридом тетрафенилфосфония. В ряде изо- и гетерополивольфраматов только анионы формы $XW_{12}O_{40}^{(8-n)}O$ (где *n* окислительное число от X) осаждаются этим реагентом. Реакция количественная и ею можно пользоваться для выделения додекавольфрамата из смеси вольфраматанионов. Использованием хлорида тетрафенилфосфония в качестве специфического реагента для додекавольфрамата удалось показать что в конденсации вольфрамата натрия при высоких концентрациях кислоты додекавольфрамат появляется при pH $\sim$ 6 и что весь вольфрамат присутствует в этой форме при pH $\sim$ 2. Факторы как на пример разбавление, время и температура так же влияют на образование додекавольфрамата в этой области pH. Реакцией пользовались для определения ряда додекавольфраматов.

РЕАКЦИИ ЭРИОХРОМ СИНЕ-ЧЁРНОГО Я:

G. L. Silver and R. C. Bowman, *Talanta*, 1967, **14**, 893.

Резюме—Приведены в форме таблицм реакции эриохром сине-чёрного R с около 25 металлов. Описаны фотометрические титрации молибдена и урана и предложен новый метод титрования тулия с ЭДТА.

ПРИМЕНЕНИЕ КРИВЫХ ВОЗБУЖДЕНИЯ И УЛЕТУЧИВАНИЯ В РАЗРАБОТКЕ УСЛОВИЙ ДЛЯ СПЕКТРОХИМИЧЕСКОГО АНАЛИЗА ОКИСИ ТАНТАЛА:

J. Brll and J. Vinot, *Talanta*, 1967, **14**, 897.

Резюме—Определение оптимальных условий для спектрографического анализа окиси тантала облегчано рассмотрением кривых улетучивания анализируемых элементов. Методом пользовались для оценки Cr, Fe, Hf, Ni, Nb, Ti, Y и Zr в области 10–1000 частей на миллион.

Potentiometric study of complexes of lead(II) with dithiocarbaminoacetic acid: O. BUDEVSKY and E. PLATIKANOVA, *Talanta*, 1967, **14**, 901 (Bulgarian Academy of Sciences, Institute of General and Inorganic Chemistry, Sofia 13, Bulgaria).

Summary—A potentiometric determination of the stability constants of lead(II)–dithiocarbaminoacetic acid complexes has been made. Potentiometric data have been used for estimating the maximum number of co-ordinated ligands. After graphical solution of the Fronaeus integral, the relationship between the concentration variables has been found, and the curve-fitting method, in which both variables are normalised, has been used for determining the stability constants. The values found are $\log \beta_1 = 7{\cdot}32 \pm 0{\cdot}12$ and $\log \beta_2 = 13{\cdot}03 \pm 0{\cdot}20$ ($\mu = 0{\cdot}1$; 25°). From these data, the relationship between the conditional stability constant $\log \beta_2'$ and pH has been calculated, thus furnishing a full description of TCA as a masking agent for lead ions.

Metal chelate exchange in the organic phase—I. Theory: Application in spectrophotometry and complex chemistry: JAROMÍR RŮŽIČKA and JIŘÍ STARÝ, *Talanta*, 1967, **14**, 909 (Department of Nuclear Chemistry, Faculty of Technical and Nuclear Physics, Prague 1, Břehová 7, Czechoslovakia).

Summary—Metal chelates, extracted from an aqueous phase by organic solvents, can react with other chelating agents (or their metal chelates) dissolved in the same solvent. This exchange of metal chelates in the organic phase can be used for (1) investigation of the exchange equilibrium and composition of the metal chelates formed, (2) determination of the extraction constants, (3) preparation of new inner-complexes soluble in organic solvents, and (4) spectrophotometric determination of small amounts of metals. The theory and experimental verification of this phenomenon are given. The extraction constants of silver and zinc diethyldithiocarbamates in carbon tetrachloride have been determined by means of the extraction constants of the corresponding dithizonates. A mixed complex of arsenic(III) with dithizone and diethyldithiocarbamic acid has been prepared and its properties studied. A simple method for spectrophotometric determination of microgram quantities of arsenic is proposed.

Spectrophotometric determination of hexafluoroarsenate with ferroin: VERNON S. ARCHER and FRANKLIN G. DOOLITTLE, *Talanta*, 1967, **14**, 921 (Department of Chemistry, University of Wyoming, Laramie, Wyoming, U.S.A.).

Summary—A spectrophotometric method for the hexafluoroarsenate anion is described. The determination involves selective extraction of the tris(1,10-phenanthroline)iron(II) salt of the anion into n-butyronitrile, followed by measurement of the absorbance of the organic layer. The extracts give good Beer's law plots over a wide range of concentrations and more than 98% of the hexafluoroarsenate is removed in a single extraction. Interference studies were made on a number of anions.

ПОТЕНЦИОМЕТРИЧЕСКОЕ ИЗУЧЕНИЕ КОМПЛЕКСОВ СВИНЦА(II) И ДИТИОКАРБАМИНОУКСУСНОЙ КИСЛОТЫ:

O. Budevsky and E. Platikanova, *Talanta*, 1967, **14**, 901

Резюме—Определены потенциометрическим методом константы устойчивости комплексов свинца(II) и дитиокарбаминоуксусной кислоты. Потенциометрические данные использованы для определения максимального числа координированных лигандов. Отношение между переменными величинами концентрации получено на основе графического решения интеграла Фронеуса, а метод приспособления кривой—с нормализированными обеими переменными величинами—использован для определения констант устойчивости. Получены величины $\log \beta_1 = 7{,}32 \pm 0{,}12$ и $\log \beta_2 = 13{,}03 \pm 0{,}20$ ($\mu = 0{,}1$; 25°). На основе этих данных определена зависимость условной константы устойчивости $\log \beta_2'$ от pH, получая этим образом совершенное охарактеризование дитиокарбаминоуксусной кислоты в качестве маскирующего агента для ионов свинца.

ОБМЕН ХЕЛАТОВ МЕТАЛЛОВ В ОРГАНИЧЕСКОЙ ФАЗЕ—I. ТЕОРИЯ : ПРИМЕНЕНИЕ В СПЕКТРОФОТОМЕТРИИ И ХИМИИ КОМПЛЕКСНЫХ СОЕДИНЕНИЙ:

Jaromír Růžička and Jiří Starý, *Talanta*, 1967, **14**, 909.

Резюме—Экстрагированные органическим растворителем из водной фазы хелаты металлов могут реагировать с другими комплексообразующими агентами (или их хелатами металлов), растворенными в том же растворителе. Этим обменом хелатов металлов в органической фазе можно пользоваться для I) исследования равновесия обмена и состава образованных хелатов металлов, (2) определения констант экстракции, (3) приготовления новых растворимых в органических растворителях внутренных комплексов, и (4) спектрофотометрического определения небольших количеств металлов. Приведены теория и экспериментальная проверка этого явления. Константы экстракции диэтилдитиокарбаминатов серебра и цинка в четыреххлорцстои чллероче определены на основе констант экстракции их дитизонатов. Приготовлен смешанный комплекс мышьяка(III) с дитизоном и диэтилдитиокарбаминовой кислотой и исследованы его свойства. Предложен цростой метод спектрофотометрического определения микрограммовых количеств мышьяка.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ГЕКСАФТОРАРСЕНАТА ФЕРРОИНОМ:

Vernon S. Archer and Franklin G. Doolittle, *Talanta*, 1967, **14**, 921

Резюме—Описан спектрофотометрический метод определения гексафторарсенатаниона. Определение основывается на селективной экстракции соли аниона с трис(1,10-фенантролин)железом(II) н-бутиронитрилом и измерении светопоглощения органического слоя. Экстракты сохраняют закон Бера в широких пределах концентрации, а больше чем 98% гексафторарсената экстрагируется в одной экстракции. Изучено влияние ряда анионов на определение.

Polarographic study of inhibitors and catalysts for the reaction of dissolved oxygen with sulphite ion: YECHESKEL ISRAEL, AVRAHAM VROMEN and BRUNO PASCHKES, *Talanta*, 1967, **14**, 925 (Israel Mining Industries, Institute for Research and Development, P.O. Box 313, Haifa, Israel).

Summary—Oxygen reduction waves are utilized to determine the inhibition effect of some reagents commonly added in polarographic work, on the reaction of dissolved oxygen with sodium sulphite in neutral and alkaline supporting electrolytes. Alkali metal hydroxides, EDTA, TEA, ethanol and methyl cellosolve inhibited the reaction to various extents. In this work, it appeared that some metallic ions, such as cobalt(II) and manganese(II) can catalyse the oxygen–sulphite reaction, enabling wider application to be made of sodium sulphite for de-oxygenation of neutral and alkaline supporting electrolytes containing inhibitors.

Determination of traces of calcium in phosphoric acid and its salts by atomic-absorption spectrometry: MASAAKI YANAGISAWA, MASAMI SUZUKI and TSUGIO TAKEUCHI, *Talanta*, 1967, **14**, 933 (Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan).

Summary—A method for the determination of traces of calcium by atomic-absorption spectrometry after extraction into an organic solvent, has been investigated for the determination of traces of calcium in phosphoric acid and its salts. Calcium is extracted as the hydroxyquinolate complex, the extract is introduced into the flame, and the calcium atomic-absorption is measured. The effects of pH, concentration of reagent, and diverse ions on the calcium extraction were investigated.

Homogeneous nucleation of magnesium hydroxide: DAVID H. KLEIN, MELVIN D. SMITH and JAMES A. DRIY, *Talanta*, 1967, **14**, 937 (Department of Chemistry, Hope College, Holland, Michigan, U.S.A.).

Summary—The rate of homogeneous nucleation of magnesium hydroxide has been determined as a function of solution concentration, using a quasi-homogeneous precipitation technique and electronic particle counting. The nucleation rate becomes measurable at supersaturations of about 4, and is dependent on the 33rd power of the product $a_{Mg}a_{OH}^2$. The experimental results are consistent with nucleation theory. The nucleus–solution interfacial energy is calculated to be 115 erg/cm^2.

ПОЛЯРОГРАФИЧЕСКОЕ ИЗУЧЕНИЕ ИНГИБИТОРОВ И КАТАЛИЗАТОРОВ ДЛЯ РЕАКЦИИ РАСТВОРЕННОГО КИСЛОРОДА С СУЛЬФИТИОНОМ:

YECHESKEL ISRAEL, AVRAHAM VROMEN and BRUNO PASCHKES, *Talanta*, 1967, **14**, 925.

Резюме—Волны восстановления кислорода использованы в определении эффекта замедления некоторых реагентов, обычно добавленных в полярографической работе, на реакцию растворенного кислорода с сульфитом натрия в нейтральных и щелочных фоновых электролитах. Гидроокиси щелочных металлов, ЭДТА, ТЭА, этиловый спирт и метилцеллосолв замедляют реакцию в различной степени. В этой работе показано, что некоторые ионы металлов, на пример кобальт(II) и марганец(II) могут катализировать реакцию кислорода с сульфитионом; этим образом дана возможность использования в большой мере сульфита натрия для обескислорожи-вания содержающих ингибиторы нейтральных и щелочных фоновых электролитов.

ОПРЕДЕЛЕНИЕ СЛЕДОВ КАЛЬЦИЯ В ФОСФОРНОЙ КИСЛОТЕ И ЕЁ СОЛЯХ МЕТОДОМ АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОМЕТРИИ:

MASAAKI YANAGISAWA, MASAMI SUZUKI and TSUGIO TAKEUCHI, *Talanta*, 1967, **14**, 933.

Резюме—Разработан метод определения следов кальция в фосфорной кислоте и её солях, основывающийся на атомно-абсорбционной спектрометрии после извлечения кальция органическим растворителем. Кальций экстрагируют в форме его комплекса с 8-оксихинолином, экстракт вводят в пламя и измеряют атомное поглощение. Изучено влияние pH, концентрации реагента и различных ионов на экстрагирование кальция.

ГОМОГЕННАЯ НУКЛЕАЦИЯ ГИДРООКИСИ МАГНИЯ:

DAVID H. KLEIN, MELVIN D. SMITH and JAMES A. DRIY, *Talanta*, 1967, **14**, 937.

Резюме—Определена скорость гомогенной нуклеации гидроокиси магния в зависимости от концентрации раствора, пользуясь квазигомогенным осаждением и электронным прибором для счета частиц. Скорость нуклеации становится измеримом при пересыщении раствора около 4 и зависит от 33 ей степени продукта $a_{Mg}a_{OH}^2$. Экспериментальные данные соглашаются с теорией нуклеации. Енергия межфазового взаимодействия между центром кристаллизации и раствором найдена 115 эрг/см^2.

Spectrophotometric determination of nitrate with *p*-diaminodiphenylsulphone and diphenylamine–*p*-diaminodiphenylsulphone: E. SZEKELY, *Talanta*, 1967, **14**, 941 (The Negev Institute for Arid Zone Research, Beer Sheva, Israel).

Summary—*p*-Diaminodiphenylsulphone is used in a new spectrophotometric method for the determination of nitrate. Factors affecting the colour development are given. The useful range for a 1-cm cell is 30–300 mg/l. In this range the coloured solutions are stable and obey Beer's law. The method is rapid and precise and is applicable to routine analysis of samples containing macro amounts of nitrates. For determination of micro amounts of nitrate the reagent is modified by addition of diphenylamine. The limit of determination is then 0·25 mg/l. at 15°. This method can be considered specific for nitrate and is applicable in the presence of nitrite.

Radiochemical separation of strontium by isotopic exchange: J. H. QURESHI, M. S. SHAHID and S. M. HASANY, *Talanta*, 1967, **14**, 951 (Atomic Energy Centre, Ferozepur Road, Lahore, Pakistan).

Summary—Isotopic exchange has been used for the rapid separation of minute quantities of radio-strontium. A number of variables such as agitation time, concentration of strontium in both phases, mode of preparation and aging of the precipitates, were studied and optimized. With an optimized procedure, exchange yields of 96% and 94% respectively were obtained when strontium sulphate and strontium oxalate precipitates were used for the exchange. Decontamination studies made with radioactive tracers of 15 elements showed that the sulphate precipitate is more selective than the oxalate, most of the elements showing <1% contamination except ^{140}Ba–^{140}La and ^{110}Ag which show high contamination. This simple procedure has also been applied for the determination of radioactive strontium in rain-water samples.

Determination of selenium and tellurium in silver chloride and uranium oxide: B. G. RUSSELL, W. V. LUBBE, ANITA WILSON, ELAINE JONES, J. D. TAYLOR and T. W. STEELE; *Talanta*, 1967, **14**, 957 (National Institute for Metallurgy, Yale Road, Milner Park, Johannesburg, South Africa).

Summary—Methods are described for the determination of selenium and tellurium in crude silver chloride produced as a by-product of the refining of gold, and in high-purity uranium oxide. Selenium and tellurium are separated from one another as well as from the numerous other substances in the sample before they are extracted into organic solvents and determined spectrophotometrically. For the determination of selenium 3,3′-diaminobenzidine is used and for tellurium, *sym*-diphenylthiourea. A minimum of 2 ppm of each element may be determined in silver chloride and 0·3 ppm in uranium oxide. Statistical data are given to show the precision and accuracy of the methods.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ НИТРАТА П-ДИАМИНОДИФЕНИЛСУЛЬФОНОМ И СМЕСЬЮ ДИФОНИЛАМИНА И П-ДИАМИНОДИФЕНИЛСУЛЬФОНА:

E. Szekely, *Talanta*, 1967, **14**, 941.

Резюме—п-Диаминодифенилсульфон применен в новом спектрофотометрическом методе определения нитрата. Приведены факторы влияющие на образование окраски. Кюветка толщины 1 см применима в пределах 30–300 мг/л. В этих пределах окрашенные растворы устойчивые и повинуются закону Бера. Метод является быстрым и точным и им можно пользоваться в серийном анализе проб, содержающих макроколичества нитратов. Для определения микроколичеств нитрата реагенту добавляют дифениламин. Предел определения в этом случае 0,25 мг/л при 15°. Этот метод можно считать специфическим для нитрата, им можно пользоваться в присутствии нитрита.

РАДИОХИМИЧЕСКОЕ ВЫДЕЛЕНИЕ СТРОНЦИЯ ИЗОТОПНЫМ ОБМЕНОМ:

I. H. Qureshi, M. S. Shahid and S. M. Hasany, *Talanta*, 1967, **14**, 951

Резюме—Изотопный обмен использован для быстрого выделения небольших количеств радиостронция. Изучено влияние и определены оптимальние условия для времени перемешивания, концентрации стронция в обеих фазах, метода получения и старения осадков. В отобранной процедуре получены обмены 96% и 94% в случае осадков сульфата стронция и оксалата стронция, соответственно. В изучении деконтаминации с использованием радиоактивных индикаторов 15 элементов, осадок сульфата оказался более селективным чем осадок оксалата: большинство элементов показали загрязнение $<1\%$, исключая ^{140}Ba, ^{140}La, и ^{110}Ag, которые элементы показали большое загрязнение. Эта несложная процедура использована для определения радиоактивного стронция в дождевой воде.

ОПРЕДЕЛЕНИЕ СЕЛЕНА И ТЕЛЛУРА В ХЛОРИДЕ СЕРЕБРА И ОКИСИ УРАНА:

B. G. Russell, W. V. Lubbe, Anita Wilson, Elaine Jones, J. D. Taylor and T. W. Steele; *Talanta*, 1967, **14**, 957.

Резюме—Описаны методы определения селена и теллура в сыром хлориде серебра, полученном в форме побочного продукта при очищении золота, и в высокочистотной окиси урана. Селен и теллур отделяют один от другого и от других веществ в образце, затем экстрагируют органическими растворителями и определяют спектрофотометрическим методом. Для определения селена пользуются 3,3′-диаминобензидином, для определения теллура—симдифенилтиомочевиной. До 2 мкг/г каждого элемента определяют в хлориде серебра, до 0,3 мкг/г в окиси урана. Точность и воспроизводимость методов показана на основе статистических данных, приведенных в стата.

Spektrophotometrische Bestimmung von Wolfram in Molybdän: B. NEEF and H.-G. DÖGE, *Talanta*, 1967, **14**, 967 (Institut für Metallphysik und Reinstmetalle der Deutschen Akademie der Wissenschaften zu Berlin, Dresden, Deutsche Demokratische Republik).

Summary—A procedure is described for the spectrophotometric determination of traces of tungsten in molybdenum. The separation is based on the different behaviour of both elements towards reduction reagents. First the molybdenum is reduced with thioglycollic acid and extracted as molybdenum(V) thiocyanate complex. After reduction with titanium(III) chloride, tungsten is extracted as tungsten(V) thiocyanate complex, which is determined spectrophotometrically. Amounts of 0·5 μg of tungsten can be determined in 0·1–0·5 g of molybdenum.

Reduction of iridium after oxidation in fuming perchloric acid: E. JACKSON and D. A. PANTONY, *Talanta*, 1967, **14**, 973 (Department of Metallurgy, Imperial College, London, S.W.7).

Summary—Evidence is given in support of the theory that high results obtained for reduction titrations of iridium solutions which have been fumed with perchloric acid are due to retention in solution of volatile reduction products of the acid.

Spectrophotometric determination of cobalt with phenanthrenequinone monoxime: K. C. TRIKHA, MOHAN KATYAL and R. P. SINGH, *Talanta*, 1967, **14**, 977 (Department of Chemistry, University of Delhi, Delhi-7, India).

Summary—Phenanthrenequinone monoxime reacts with cobalt to form a yellow–orange insoluble 1:3 (cobalt:ligand) complex which is extractable into chloroform in the pH range 4·45–8·0. The determination of cobalt is carried out at 470 mμ. Beer's law is obeyed over the concentration range 0–3·0 ppm of cobalt. The sensitivity is 0·00336 μg of Co/cm^2 for 0·001 absorbance. The effect of a number of foreign ions has been studied.

Determination of sorbic acid with sodium chlorite: P. SPACU and H. DUMITRESCU, *Talanta*, 1967, **14**, 981 (Department of Inorganic Chemistry, University of Bucharest, Splaiul Independentei 89, Bucharest, Rumania).

Summary—A new method for the determination of sorbic acid is proposed, using sodium chlorite in hydrochloric acid medium as reagent. In these conditions the hydrochloric acid is oxidized to chlorine which adds on to the double bonds of the sorbic acid. The addition is rapid (30–90 sec) and for this reason the determination is more rapid then others similar to it. Sorbic acid has been determined in foods by this method, after a preliminary solvent extraction or steam-distillation.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ВОЛЬФРАМА В МОЛИБДЕНЕ:

B. Neef and H.-G. Döge, *Talanta*, 1967, **14**, 967.

Резюме—Описан метод спектрофотометрического определения следов вольфрама в молибдене. Разделение основывается на различном поведении этих элементов в присутствии восстановителей. Сперва молибден восстанавливается тиогликолевой кислотой и экстрагируется в форме тиоцианата молибдена(V). После восстановления с хлоридом титана(III) вольфрам экстрагируют в форме комплекса тиоцианата вольфрама(V), который затем определяют спектрофотометрическим методом. Этим методом можно определять 0,5 мкг вольфрама в 0,1–0,5 г молибдена.

ВОССТАНОВЛЕНИЕ ИРИДИЯ ПОСЛЕ ОКИСЛЕНИЯ В ДЫМЯЩЕЙСЯ ХЛОРНОЙ КИСЛОТЕ:

E. Jackson and D. A. Pantony, *Talanta*, 1967, **14**, 973.

Резюме—Приведены данные, поддерживающие теорию что высокие результаты полученные в восстановительном титровании растворов иридия, обработанных дымящейся хлорной кислотой являются в результате удерживания в растворе летучих продуктов восстановления кислоты.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ КОБАЛЬТА ФЕНАНТРЕНХИНОНМОНОКСИМОМ:

K. C. Trikha, Mohan Katyal and R. P. Singh, *Talanta* 1967, **14**, 977.

Резюме—Фенантренхинонмоноксим реагирует с кобальтом образуя оранжевожёлтый 1 : 3 (кобальт : лиганд) комплекс, экстрагируемый хлороформом в области pH 4,45–8,0. Определение кобальта проводится при 470 ммк. Закон Бера почитается в области концентрации 0–3,0 мг/л. Чувствительность 0,00336 мкг кобальта/см^2 для поглощения 0,001. Изучено влияние ряда посторонных ионов.

ОПРЕДЕЛЕНИЕ СОРБИНОВОЙ КИСЛОТЫ ХЛОРИТОМ НАТРИЯ:

P. Spacu and H. Dumitrescu, *Talanta*, 1967, **14**, 981.

Резюме—Предложен новый метод определения сорбиновой кислоты с использованием хлорита натрия в солянокислом растворе в качестве реагента. В этих условиях соляная кислота окисляется в хлор, который присоединяется по месту двойных связей сорбиновой кислоты. Присоединение протекает быстро (30–90 сек.), поэтому определение быстрее чем остальные. Сорбиновую кислоту определяли этим методом в пищах, после предварительной экстракции или перегонки с водяным паром.

Decomposition of thiosulphate in acidified oxidants: G. W. LATIMER, JR. and ELAINE I. STEICKO, *Talanta*, 1967, **14**, 984 (Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, U.S.A.).

Summary—The Wollack procedure has been used to study the competition between oxidant and acid for the thiosulphate ion. In concentrated hydrochloric acid solutions of iodine, iodate and chloramine-T, polythionates are the chief products, whereas in acid permanganate substantial amounts of other products occur. Both the concentration of the acid and the acid anion affect the course of the reaction in these solutions. Production of polythionate, an acid-decomposition product, suggests that acid decomposition successfully competes with oxidation.

Interfacial free energies of ionic crystals: G. CLEGG and T. P. MELIA, *Talanta*, 1967, **14**, 989 (Department of Chemistry and Applied Chemistry, University of Salford, Salford 5, U.K.).

Summary—Minimum values of the liquid–crystal interfacial free energy have been obtained from data on the maximum supercooling of small droplets of solutions of ionic crystals.

РАЗДОЖЕНИЕ ТИОСЧЛЬФАТА В КИСЛЫХ РАСТВОРАХ ОКИСЛИТЕЛЕЙ:

G. W. Latimer, Jr. and Elaine I. Stetcko, *Talanta*, 1967, **14**, 984.

Резюме—Процедура Воллака применена в изучении конкуренции окислителя и кислоты для тиосульфатиона. В сильно солянокислых растворах иода, иодата и хлорамина Т, главными продуктами являются политионаты, тогда как в кислом растворе перманганата образуются значительные количества других продуктов. Как концентрация кислоты так и анион кислоты влияют на течение реакции в этих растворах. Образование политионата—продукта разложения кислоты—указивает на успешную конкуренцию разложения кислоты с окислением.

МЕЖПОВЕРХНОСТНАЯ СВОБОДНАЯ ЭНЕРГИЯ ИОННЫХ КРИСТАЛЛОВ:

G. Clegg and T. P. Melia, *Talanta*, 1967, **14**, 989.

Резюме—Получены минимальные величны свободной энергии поверхности жидкость–кристалл на основе данных о максимальном переохлаждении маленких капелек растворов ионных кристаллов.

SUMMARIES FOR CARD INDEXES

A critical review of neutron activation and tracer methods for the determination of the noble metals: F. E. BEAMISH, K. S. CHUNG and A. CHOW, *Talanta*, 1967, **14**, 1. (Department of Chemistry, University of Toronto, Toronto 5, Canada).

Summary—Neutron activation methods for the seven noble metals are critically reviewed up to December, 1965. The methods deal with the determination of trace impurities in each noble metal as well as traces of noble metals in media such as organic material, fission product and other solutions, ores, alloys, minerals, silica and base metals. The need for confirmatory evidence in the case of such complex materials as ores is emphasized.

A new oxidimetric reagent: Potassium dichromate in a strong phosphoric acid medium—VI: Photometric titration of vanadium(IV) and of cerium(III) alone and in mixtures with iron(II): G. GOPALA RAO and P. KANTA RAO, *Talanta*, 1967, **14**, 33. (Department of Chemistry, Andhra University, Waltair, India).

Summary—Vanadium(IV) can be accurately titrated with potassium dichromate in media containing phosphoric acid of 3–12*M* concentration: the change in absorption of vanadium(IV) is followed in the region 660 mμ using a red filter. It is more convenient to carry out the titration in 3*M* phosphoric acid because at higher concentrations chloride, nitrate, cerium(III) and manganese(II) may interfere. Photometric titration is more convenient than potentiometric because the former can be made in a 3*M* phosphoric acid medium, whereas the latter is possible only in 12*M* phosphoric acid. The simultaneous differential photometric titration of iron(II) and vanadium(IV) is also possible. Conditions have been found for the photometric titration of cerium(III) and of cerium(III) plus iron(II). The titration is carried out (at 450 mμ or with a blue filter) in about 10.5*M* phosphoric acid. Application of the method to a cerium mineral is considered.

Separation of strontium from large amounts of calcium, with application to radiostrontium analysis: VICTOR E. NOSHKIN and NORMAN S. MOTT, *Talanta*, 1967, **14**, 45. (Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543, U.S.A.).

Summary—The elution first of calcium and then of strontium by complex formation with cyclohexanediaminetetra-acetic acid (CyDTA) after sorption on ion-exchange columns, is shown to require careful control of pH and the concentrations of CyDTA and NH_4^+. A procedure is described for volumetric analysis of calcium and strontium, and for use of this separation procedure before determination of ^{90}Sr in sea-water. Careful choice of reagents and materials is shown to be necessary for use of such a method in determination of trace amounts of radiostrontium.

КРИТИЧЕСКИЙ ОБЗОР МЕТОДОВ НЕТЙРОННОГО АКТИВАЦИОННОГО АНАЛИЗА И ИНДИКАТОРНОГО АНАЛИЗА ДЛЯ ОПРЕДЕЛЕНИЯ БЛАГОРОДНЫХ МЕТАЛЛОВ:

F. E. Beamish, K. S. Chung and A. Chow, *Talanta*, 1967, **14**, 1.

Резюме—Критически обсуждаются опубликованные до декабря 1965 г. методы нейтронного активационного анализа для определения семь благородных металлов. Методы разработаны для определения следовых примес в каждом благородном металле и следов благородных металлов в органических материалах, продуктах расщепления и других растворах, рудах, сплавах, минералах, в кварце и простых металлах. Подчеркивается нужда подкрепляющих данных в случае сложных материалов, как на пример руд.

НОВЫЙ ОКСИДИМЕТРИЧЕСКИЙ РЕАГЕНТ: БИХРОМАТ КАЛИЯ В СИЛЬНО ФОСФОРНОКИСЛОЙ СРЕДЕ—VI: ФОТОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ ВАНАДИЯ(IV), ТОЛЬКО ЦЕРИЯ(III) И ЦЕРИЯ(III) В СМЕСЯХ С ЖЕЛЕЗОМ(II):

G. Gopala Rao and P. Kanta Rao, *Talanta*, 1967, **14**, 33.

Резюме—Предложенный метод позволяет аккуратное титрование ванадия(IV) бихроматом калия в растворе содержащем фосфорную кислоту концентрации 3-12 М: перемену светопоглощения ванадия(IV) измеряют в области 660 ммк, с использованием красного фильтра. Удобнее провести титрование в 3М фосфорной кислоте, потому что при более высоких концентрациях ионы хлорида, нитрата, церия(III) и марганца(II) мешают определению. Фотометрическое титрование удобнее чем потенциометрическое потому что первое можно провести в 3М фосфорной кислоте, а второе только в 12М фосфорной кислоте. Также осуществымо одновременное дифференциальное фотометрическое титрование железа(II) и ванадия(IV). Разработаны условия для фотометрического титрования церия(III) и церия(III) в смеси с железом(II). Титрование проводится (при 450 ммк или пользуясь голубым фильтром) в 10,5М фосфорной кислоте. Предполагается использование метода в анализе руды церия.

ОТДЕЛЕНИЕ СТРОНЦИЯ ОТ БОЛЬШИХ КОЛИЧЕСТВ КАЛЬЦИЯ И ЕТО ИСПОЛЬЗОВАНИЕ В АНАЛИЗЕ РАДИОСТРОНЦИЯ:

Victor E. Noshkin and Norman S. Mott, *Talanta*, 1967, **14**, 45.

Резюме—Показано что элюирование кальция и после его стронция, путем образования комплексов с циклогексаминтетрадиаминтетрауксусной кислотой (ЦиДТА) и сорбирования на колонке ионообменника, требует тщательный контроль pH и концентраций ЦиДТА и ИН-0. Описывается процедура для обменного анализа кальция и стронция и ее использование для определения --00 в морской воде. Тщательнеый выбор реагентов и магериалов оказался необходимым при использвании этого метода для определения следовых количеств радиостронция.

Determination of rhenium in molybdenite by neutron-activation analysis: KIKUO TERADA, YUKIO YOSHIMURA, SUSUMU OSAKI and TOSHIYASU KIBA, *Talanta*, 1967, **14**, 53. (Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa, Japan.)

Summary—A neutron-activation method is described for the determination of rhenium in molybdenite. Radiochemical separation by a carrier technique was carried out very rapidly by means of successive liquid–liquid extraction processes. The recovery of rhenium, which was determined by a spectrophotometric method, was about 93%. About 10 samples could be analysed within 6 hr in parallel runs.

Electronic calculation in analytical chemistry—I: ALGOL programme for evaluation of model analyses: G. GOTTSCHALK, *Talanta*, 1967, **14**, 61. (OSRAM Studiengesellschaft Berlin, Technische Universität Berlin, Germany.)

Summary—The usual way of evaluating an analytical method is to carry out a series of model experiments. A comparison of the amount taken and the amount found gives objective numerical information about the random and systematic errors in the particular range studied. If conventional methods of calculation are used, the time needed and the difficulty are relatively large. A series of 24 tests may need 8 hr for the calculations, even if no human error in computation occurs. Experience shows that inexperienced operators may need several days for the calculations. Results free from error can be obtained in as little as 5 min by electronic computing. A calculation programme written in the universal logical language ALGOL is given. The preparatory operations are so simple that skilled assistance is not necessary.

Thermal standards in thermogravimetry: C. J. KEATTCH, *Talanta*, 1967, **14**, 77. (John Laing Research & Development Ltd., Boreham Wood, Hertfordshire, England.)

Summary—Comparisons of thermogravimetric data from different instruments have often led to controversy because of lack of appreciation that the values are influenced by the apparatus used. Consequently, it is suggested that various compounds be employed as thermal standards for comparing data from different sources. The paper also discusses the variables to be considered when attempting to devise such standards and includes a list of suggested thermal standards covering the ranges 100–400° and 1050–1060°.

ОПРЕДЕЛЕНИЕ РЕНИЯ В МОЛИБДЕНИТЕ МЕТОДОМ НЕЙТРОННОГО АКТИВАЦИОННОГО АНАЛИЗА:

Kikuo Terada, Yukio Yoshimura, Susumu Osaki and Toshiyasu Kiba, *Talanta*, 1967, **14**, 53.

Резюме—Описывается нейтронноактивационный метод для определения рения в молибдените. Радиохимическое выделение методом носителя производили очень быстро последовательным экстрагированием растворителями. Возврат рения, после определения спектрофотометрическим методом, был около 93%. В течение 6 часов можно анализировать около 10 образцов, двое по двое.

ИСПОЛЬЗОВАНИЕ ЕЛЕКТРОННОГО РАСЧЕТА В АНАЛИТИЧЕСКОЙ ХИМИИ—I: АЛГОЛ ПРОГРАММА В ОЦЕНКЕ МОДЕЛЬНЫХ АНАЛИЗОВ:

G. Gottschalk, *Talanta*, 1967, **14**, 61.

Резюме—Для оценки аналитического метода обыкновенно проводят ряд модельных опытов. Сравнение количеств взятых и полученных в анализе дает объективные численные данные о беспорядочных и систематических ошибках в исследованных пределах. Условные методы расчета трудны и требуют довольно много времени. Для расчета серии 24 опытов нужно 8 часов даже без появления ошибок в расчете. Знакомо что неопытному оператору нужно несколько дней для расчета. Методом электронного расчета получаются безошибочные результаты только через тять минут. Приведена программа расчета выраженная в универсальном логическом языке АЛГОЛ. Приготовительные работы так просты, что квалифицированная помощь не нужна.

ТЕРМИЧЕСКИЕ ЭталОНЫ В ТЕРМОГРАВИМЕТРИИ:

C. J. Keattch, *Talanta*, 1967, **14**, 77.

Резюме—Сравнение термогравиметрических данных, полученных различными приборами часто привело до дискуссии, потому что не принято во внимание что использованные приборы влияют на результаты. Ради этого предложено использование различных соединений в качестве термических эталонов для сравнения данных из различных источников. В статье тоже обсуждаются факторы влияющие на выбор таких эталонов и приводится список предложенных термических эталонов для областей 100–400° и 1050–1060°.

Application of radioisotopes in column chromatography on substituted celluloses—III: The separation of gold from silver, iron and other metals: R. A. A. MUZZARELLI, *Talanta*, 1967, **14**, 85. (Department of Chemistry, Faculty of Science, University of Sherbrooke, Sherbrooke, Québec, Canada).

Summary—The chromatographic behaviour of several metals has been studied on columns of natural and substituted celluloses, by using radioisotopes. It has been found that gram and nanogram amounts of gold are not adsorbed on natural cellulose, and consequently gold can be separated from nanogram amounts of silver, iron, zinc, cadmium, chromium, manganese and cobalt. Gold has a limited tendency to form complexes with the functional groups of the celluloses, but the other metals mentioned formed very stable complexes. The results have also been compared with those obtained for mercury.

Hydrolysis study of organic acid anhydrides by differential thermal analysis—II: Maleic anhydride and trimellitic anhydride: J. M. ROSENFELD and C. B. MURPHY, *Talanta*, 1967, **14**, 91. (General Electric Company, Schenectady, N.Y., U.S.A.).

Summary—Differential thermal analysis has been used to follow the hydrolysis of maleic anhydride (MA) and trimellitic anhydride (TMA). On exposure of MA to an atmosphere of 96% relative humidity maleic acid is produced, hydrolysis being complete in 21 hr at 22°, but no hydrolysis occurs at a relative humidity of 50%. When exposed to an atmosphere of 96% relative humidity, TMA is quite stable for short periods, but hydrolyses slowly, the production of trimellitic acid being complete in 113 hr at 22°.

Complexometric determination of gallium with Calcein Blue as indicator: H. N. ELSHEIMER, *Talanta*, 1967, **14**, 97 (U.S. Geological Survey, Menlo Park, California 94025, U.S.A.).

Summary—A metalfluorechromic indicator, Calcein Blue, has been used for the back-titration of milligram amounts of EDTA in presence of gallium complexes. The indicator was used in conjunction with an ultraviolet titration assembly equipped with a cadmium sulphide detector cell and a microammeter for enchanced end-point detection. The result is a convenient and rapid method with an accuracy approaching 0·1% and a relative standard deviation of about 0·4% for 10 mg of gallium.

ИСПОЛЬЗОВАНИЕ РАДИОИЗОТОПОВ В ХРОМАТОГРАФ́И НА КОЛОНКЕ ЗАМЕ0ОЕННЫХ ЦЕЛЛЮЛОЗ—III. ОТДЕЛЕНИЕ ЗОЛОТА ОТ СЕРЕБРА, И ДРУГИХ МЕТАЛЛОВ:

R. A. A. Muzzarelli, *Talanta*, 1966, **14**, 85.

Резюме—Определены хроматографические характеристики на колонках природной и замещенных целлюлоз ряда металлов, с использованием радиоизотопов. Результаты опытов показывают что граммовые и наногра́ммовые количества золота не адсорбиру ются на природной целлюлозе, поэтому этим методом можно пользоваться для отделения золота от наног раммовых количеств серебра, железа, цинка, кадмия, хрома, марганца и кобальта. Золото в ограниченной мере образует комплексы с функциональными группами целлюлозы, пока другие упомянутые металлы образуют очень устойчивые комплексы. Результаты опытов сравнены с полученными для ртути данными.

ИЗУЧЕНИЕ ГИДРОЛИЗА АНГИДРИДОВ ОРГА ОРГАНИЧЕСКИХ КИСЛОТ МЕТОДОМ ДИФФЕРЕНЦИАЛЬНОГО ТЕРМИЧЕСКОГО АНАЛИЗА —II: МАЛЕИНОВЫЙ АНГИДРИД И ГЕМЕЛЛИТО ВЫЙ АНГИДРИД:

J. M. Rosenfeld and C. B. Murphy, *Talanta*, 1967, **14**, 91.

Резюме—Метод дифференциального термического анали а исполь ован для и учения гидроли а малеинового (МА) и гемеллитового (ГА) ангидридов. При контакте МА с во - духом 96Ш относительной влажности обра уется малеиновая кислота, а гидроли окончен нере 21 час при 22°; гидроли не появляется при относительной влажности 50Ш. При контакте с во духом 96Ш тной относительной влажности ТА довольно устойчивый в коротком интервале времени, но постепенно гидроли ируется, а обра ование гемеллитовой кислоты окончано чере 113 часа.

КОМПЛЕКСОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ГАЛЛИЯ С ИСПОЛЬЗОВАНИЕМ КАЛЬЦЕИНОВОГО ГОЛУБОГО В КАЧЕСТВЕ ИНДИКАТОРА:

H. N. Elsheimer *Talanta*, 1967, **14**, 97.

Резюме—Автор пользовался металлофлуорохромным индикаторомкальцеиновым голубым—для титрования миллиграммовых количеств галлия в форме комплексов с ЭДТА. Индикатор использован на приборе для титрования в ультрафиолетовом свете, снабженному с детектором на основании сульфида кадмия и микро амперметром для улучшенного открития конца титрования. Разработанный подходящий и быстрый метод имеет точност около 0,1% и относительную стандартную ошибку 0,4% для 10 мг галлия.

Fluorescence and phosphorescence characteristics of anticoagulants: A new approach to direct measurement of drugs in whole blood: H. C. HOLLIFIELD and J. D. WINEFORDNER, *Talanta*, 1967, **14**, 103. (University of Florida, Department of Chemistry, Gainsville, Florida 32601, U.S.A.)

Summary—Fluorimetric and phosphorimetric excitation and emission peaks and limiting detectable concentrations and phosphorimetric decay times are given for warfarin, dicumarol, diphenandione, phenindione and tromexan. Known concentrations of warfarin, a highly fluorescent compound, and dicumarol, a highly phosphorescent compound, are directly measured in the complex biochemical system of whole blood. Excellent recoveries of warfarin and dicumarol in the concentration range of 0·1 to 10 mg% in whole blood were achieved.

Substoichiometric separation in activation analysis: Extraction of co-ordinatively-unsolvated salts: I. P. ALIMARIN and G. A. PEREZHOGIN, *Talanta*, 1967, **14**, 109. (V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, Moscow, U.S.S.R.)

Summary—The necessary conditions have been examined for the use of extraction of coordinatively-unsolvated salts for substoichiometric separations in activation analysis, especially the influence of interfering ions and of the concentration of the carrier. A study has been made of the substoichiometric extraction of halide ions, oxyanions and anionic metal complexes by means of the tetraphenylarsonium ion into chloroform and dichloroethane, and of the extraction of alkali metal ions into nitrobenzene with tetraphenylborate. Substoichiometric extraction can be combined with neutron-activation analysis for the determination of traces of iodine, caesium, rubidium, manganese, rhenium, chromium, thallium, gold, gallium and tantalum.

Purification des colorants thiaziniques, Azur A, Azur B, Azur C, par une methode de partage: ROLAND BONNEAU, JEAN FAURE and JACQUES JOUSSOT-DUBIEN, *Talanta*, 1967, **14**, 121. (Département de Chimie-Physique, Faculté des Sciences de Bordeaux, France.)

Summary—Some *N*-methylated derivatives of thionine have been separated from thionine, Methylene Blue, and each other by solvent extraction into carbon tetrachloride from an aqueous solution buffered to the pH appropriate for each compound. The method can be used to purify the dyes.

ФЛУОРЕСЦЕНТНЫЕ И ФОСФОРЕСЦЕНТНЫЕ ХАРАКТЕРИСТИКИ ПРОТИВОСВЕРТЫВАЮЩИХ СРЕДСТВ: НОВЫЙ ПОДХОД К ПРЯМОМУ ОПРЕДЕЛЕНИЮ ЛЕКАРСТВЕННЫХ ПРЕПАРАТОВ В ЦЕЛЬНОЙ КРОВИ:

H. C. Hollifield and J. D. Winefordner, *Talanta*, 1967, **14**, 103.

Резюме—Приведены флуориметрические и фосфорометрические пики во буждения и змиссии, предельные концентрина, дикумарола, дифенандиона, фениндиона и тромексана. И вестные концентрации уорфарина—сильно флуоресцирующего соединения, и дикумарола—сильно фосфоресцирующего соединения определяют прямо в сложной биохимической системе цельной крови. Получены отличные выходы для уорфарина и дикумарола в пределах концентрации от 0,1 до 10 мг 00 в цельной.

СУБСТЕХИОМЕТРИЧЕСКОЕ РАЗАЕЛЕНИЕ В АКТИВАЦИОННОМ АНАЛИЗЕ ПУТЕМ ЭКСТРАКЦИИ КООРДИНАЦИОННО НЕСОЛЬВАТИРОВАННЫХ СОЛЕЙ

I. P. Alimarin and G. A. Perezhogin, *Talanta*, 1967, **14**, 109.

Резюме—Рассмотрены условия субстехиометрического разделения в активационном анализе путем экстракции координационно несольватированных солей, влияние концентрации носителя и мешающих ионов. Изучена субстехиометрическая экстракция галогенид-ионов, кислородсодержащих анионов и комплексных металлсодержащих анионов с тетрафениларсонием хлороформом или дихлорэтаном, а также катионов щелочных металлов с тетрафенилбораторм нитробензолом. Субстехиометрическое экстракционное разделение йода, цезия рубидия, марганца, рения, хрома, таллия, золота, галлия, тантала может быть использовано для нейтроноактивационного определения следов этих элементов.

ОЧИСТКА ТИАЗИНОВЫХ КРАСОК АЗУРА А, АЗУРА В И АЗУРА С МЕТОДОМ ЭКСТРАКЦИИ РАСТВОРИТЕЛЕМ:

Roland Bonneau, Jean Faure and Jacques Joussot-Dubien, *Talanta*, 1967, **14**, 121.

Резюме—Авторы отделили некоторые *N*-метилированные производные тионина от тионина, метиленового голубого и одного от другого экстрагированием тетрахлорметаном из водного раствора забуферированного до pH, ответствующем каждому соединению. Методом можно пользоваться для очистки красок.

Azo dyes from 2-amino-1,3,4-thiodiazole: F. H. POLLARD, G. NICKLESS and T. J. SAMUELSON, *Talanta*, 1967, **14**, 123. (Department of Inorganic Chemistry, School of Chemistry, The University, Bristol 8, England).

Summary—Thiodiazolyazo dyes from resorcinol, *p*-cresol and *β*-naphthol have been prepared. They are inferior to their thiazole and triazole analogues in their colour-forming reactions with metal ions.

Semimicro method for the determination of linalol in coriander oil: K. R. MANOLOV and E. V. GEORGIEV, *Talanta*, 1967, **14**, 124. (Higher Institute of Food Industry, Department of Inorganic and Analytical Chemistry, Plovdiv, Bulgaria).

Summary—Linalol has been determined colorimetrically in essential oils by means of the green colour developed in the presence of nitrous acid. Geraniol, dipentene, terpineol, citronellol and citral also give a green colour, and are therefore calculated as linalol by this method, but the error is small if they are present in small concentrations.

Photo-induced oxidation of some organic carbonyl compounds by vanadium(V): K. S. PANWAR and J. N. GAUR, *Talanta*, 1967, **14**, 127. (Department of Chemistry, University of Rajasthan, Jaipur, India).

Summary—The oxidation of pyruvic acid, levulinic acid, acetaldehyde, isobutyraldehyde, and acetylacetone by vanadium(V) in aqueous solution on illumination with visible light is described. Pyruvic acid undergoes oxidation much more rapidly than does levulinic acid; both give acetic acid. Acetaldehyde is more rapidly oxidized than is isobutyraldehyde, the former giving formic acid, and the latter, formic acid and acetone. Acetylacetone is converted into acetic acid. The oxidations are rapid and quantitative and may be used for the estimation of these carbonyl compounds.

Amalgam exchange separation of radiothallium: RICHARD B. HAHN and GEORGE M. KANAPILLY, *Talanta*, 1967, **14**, 129. (Chemistry Department, Wayne State University, Detroit, Michigan 48202, U.S.A.).

Summary—A method is presented for the rapid separation of radiothallium. The solution is made basic by addition of ammonia, then sodium fluoride and ethylenediamine are added and the mixture is shaken with 3% thallium amalgam. A rapid exchange takes place and the bulk of the activity is concentrated in the amalgam. The amalgam is diluted with clean mercury and shaken with acidic cobalt nitrate solution which back-extracts thallium. About 90% of the thallium activity is recovered.

АЗОКРАСИТЕЛИ НА ОСНОВЕ 2-АМИНО-1,3,4-ТИОДИАЗОЛА:

F. H. POLLARD, G. NICKLESS and T. J. SAMUELSON, 1967, **14**, 123.

Резюме—Приготовлены тиодиазолилазокрасители из резорцина, п-крезола и β-нафтола. Цветообразующие реакции этих красителей с ионами металлов не так успешны как аналогичных красителей на основе тиазола и триазола.

K. R. MANOLOV and E. V. GEORGIEV, *Talanta*, 1967, **14**, 124.

Резюме—Пиналоол в эфирных маслах определен колориметрическим методом, основывающимся на зеленой окраске которая образуется в присутствии азотистой кислоты. Гераниол, дипентен, терпинеол, цитронеллол и цитрал также дают зеленую окраску и поэтому в этом методе определяются вместе с линалоолом; однако, ошибка небольшая если эти соединения присутствуют только в небольших концентрациях

ФОТОИНДУКТИРОВАННОЕ ОКИСЛЕНИЕ ВАНАДИЕМ(V) НЕКОТОРЫХ ОРГАНИЧЕСКИХ КАРБОНИЛЬНЫХ СОЕДИНЕНИЙ:

K. S. PANWAR and J. N. GAUR, *Talanta*, 1967, **14**, 127.

Резюме—Описывается окисление пировиноградной, илевулиновой кислот, ацетальдегида, изомасляного альдегида и ацетилацетона в водном растворе, с использованием ванадия(V) и облучения видимым светом. Пировиноградная кислота окисляется гораздо быстрее чем левулиновая кислота; продуктом окисления в обоих случаях является уксусная кислота. Ацетальдегид окисляется быстрее чем изомасляный альдегид: первый дает муравьиную кислоту а второй—муравьиную кислоту и ацетон. Ацетилацетон превращается в уксусную кислоту. Эти процедуры показываются быстрыми и количественными, ими можно пользоваться для определения этих карбонильных соединений.

ВЫДЕЛЕНИЕ РАДИОТАЛЛИЯ С ИСПОЛЬЗОВАНИЕМ АМАЛЬГАМНОГО ОБМЕНА:

RICHARD B. HAHN and GEORGE M. KANAPILLY, *Talanta*, 1967, **14**, 129.

Резюме—Предложен метод для быстрого выделения радиоталлия. Раствору прибавляют аммиак до щелочной реакции, затем фторид натрия и этилендиамин и раствор встряхивают 3% тной амальгамой таллия. Происходит быстрый обмен и основная масса радиоталлия концентрируется в амальгаме. Амальгаму разбавляют чистой ртутью и встряхивают кислым раствором нитрата кобальта для экстрагирования. Выход радиоактивного таллия около 90%.

High frequency titration methods in the investigation of complex formation: D. I. RYABCHIKOV and V. A. ZARINSKY, *Talanta*, 1967, **14**, 133. (Vernadsky Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, Moscow, U.S.S.R.)

Summary—High frequency titration is a valuable tool in the study of complex formation in solutions, and the breaks in the titration curves can be used, in conjunction with the results of other physical methods, to determine the composition of the complexes formed. High frequency titration and other methods have been used to study the complexes formed by thorium, indium, plutonium(V), and boron with various complexing agents, and to develop methods for the determination of thorium and yttrium in rare earth mixtures, and of indium in the presence of zinc, cadmium, aluminium, nickel and cobalt.

Application of the drop method to the study of nucleation of sparingly soluble chelates: S. THOMPSON and L. GORDON, *Talanta*, 1967, **14**, 137. (Department of Chemistry, Case Institute of Technology, Cleveland, Ohio 44106, U.S.A.)

Summary—The methods of producing supersaturated solutions of sparingly soluble chelates by precipitation from homogeneous solution have been combined with drop nucleation studies.

Precipitation from homogeneous solution applied to the drop technique for the study of nucleation: O. E. HILEMAN, JR., *Talanta*, 1967, **14**, 139. (Department of Chemistry, Burke Chemical Laboratories, McMaster University, Hamilton, Ontario, Canada.)

Summary—The technique of precipitation from homogeneous solution has been successfully coupled with the drop technique for study of the nucleation process.

ИСПОЛЬЗОВАНИЕ МЕТОДОВ ВЫСОКОЧАСТОТНОГО ТИТРОВАНИЯ ДЛЯ ИЗУЧЕНИЯ КОМПЛЕКСООБРАЗОВАНИЯ:

D. I. Ryabchikov and V. A. Zarinsky, *Talanta*, 1967, **14**, 133.

Резюме—Метод высокочастотного титрования является очень полезным в изучении образования комплексов в растворе; изломом кривой титрования можно пользоваться—вместе с результатами других физических методов—для определения состава образованных комплексов. Метод высокочастотного титрования и другие методы были использованы для изучения комплексов тория, индия, плутония(V) и бора с различными комплексообразующими агентами и для разработки методов для определения тория и иттрия в смесях редкоземельных элементов, и индия в присутствии цинка, кадмия, алюминия, никеля и кобальта.

ИСПОЛЬЗОВАНИЕ КАПЕЛЬНОГО МЕТОДА В ИЗУЧЕНИИ НУКЛЕАЦИИ УМЕРЕННО РАСТВОРИМЫХ ХЕЛАТОВ:

S. Thompson and L. Gordon, *Talanta*, 1967, **14**, 137.

Резюме—Исследовано приготовление пересыщенных растворов умеренно растворимых хелатов методом осаждения из гомогенного раствора, вместе с изучением нуклеации капельным методом.

ПРИМЕНЕНИЕ ОСАЖДЕНИЯ ИЗ ГОМОГЕННОГО РАСТВОРА НА КАПЕЛЬНЫЙ МЕТОД С ЦЕЛЬЮ ИЗУЧЕНИЯ НУКЛЕАЦИИ:

O. E. Hileman, *Talanta*, 1967, **14**, 139.

Резюме—Осаждение изгомогенного раствора успешно использовано вместе с капельным методом для изучения процесса нуклеации.

Determination of trace amounts of sulphur in selenium: BRITT-LOUISE SJÖBORG, *Talanta*, 1967, **14**, 693 (Department of Analytical Chemistry, University of Uppsala, Uppsala, Sweden).

Summary—Determination of trace amounts of sulphur as Methylene Blue after reduction of sulphate to sulphide by hydriodic and hypophosphorous acids in acetic acid solution is applied to the determination of trace amounts of sulphur in selenium after removal of the selenium by evaporation with hydrobromic acid. Samples of 100 mg or less of selenium are chosen if the sulphur content is greater than 5–10 ppm; the time required for the separation is about 1·5 hr; 100 ppm of sulphur has been determined with a coefficient of variation of 5·2%. If the sulphur content is less than 5 ppm, 1-g samples must be taken and the time required is then about 3 hr; 0·4 ppm of sulphur has been determined with a standard deviation of 0·13 ppm. The accuracy of the method seems to be well within the random error.

Tetrachlorogallate(III) complexes with basic triphenylmethane and diphenylnaphthylmethane dyestuffs: V. ARMEANU and P. COSTINESCU, *Talanta*, 1967, **14**, 699 (Chemistry and Physics Department, V. I. Lenin Institute for Economic Sciences, 6 Piaţa Romană, Bucharest, Romania, and Department of Inorganic and Analytical Chemistry, Institute for Petroleum, Gas and Geology, 6 Traian Vuia St., Bucharest).

Summary—A general survey is given of the properties of tetrachlorogallate(III) complexes with basic dyestuffs of the triphenylmethane and diphenylnaphthylmethane class; solvents for extraction, the absorption spectra and molar absorptivities, the optimum concentrations of the dyestuffs and of hydrochloric acid, the stability of the compounds and their composition are also described. Analytical methods for the determination of traces of gallium by means of many of these complexes are suggested.

Estimation of the minimum detectable concentration and optimum instrumental conditions in precision absorption spectrophotometry of substances in the condensed phase: J. J. CETORELLI and J. D. WINEFORDNER, *Talanta*, 1967, **14**, 705 (Department of Chemistry, University of Florida, Gainesville, Florida 32601, U.S.A.).

Summary—An expression for the signal-to-noise ratio in precision absorption spectrophotometry of molecules in the condensed phase is derived and used to calculate the theoretical minimum detectable sample concentration, C_{mt} and to predict the best instrumental conditions for measurement. Single-beam and double-beam instruments are considered. The theoretically calculated values of C_{mt} for several organic molecules are compared with the practical minimum detectable sample concentrations, C_{mp}, which are those concentrations giving an absorbance of 0·002. As long as the source of radiation is intense, and the root-mean-square noise-to-signal ratio for incident radiation passing through the blank is known, then the expression for C_{mt} is extremely simple and easy to evaluate for any given substance whose molar absorptivity is known. The influence of instrumental parameters on the value of C_{mt} is evaluated, and only the monochromator slitwidth, the number of combined blank and sample signal measurements, and the frequency response bandwidth of the electrometer-readout system have any significant effect on the value of C_{mt} (for any given wavelength setting of the monochromator).

ОПРЕДЕЛЕНИЕ СЛЕДОВЫХ КОЛИЧЕСТВ СЕРЫ В СЕЛЕНЕ:

BRITT-LOUISE SJÖBORG, *Talanta*, 1967, **14**, 693.

Резюме—Определение следовых количеств серы в форме метиленовой сини после восстановления сульфата до сульфида раствором иодстоводородной и гипофосфористой кислотах в уксусной кислоте, применено на определение следовых количеств серы в селене, после удаления селена выпариванием с бромистоводородной кислотой. Если содержание серы превышает 5–10 мкг/г, отбирают пробу селена 100 мг или менее; продолжительность отделения около полутора часов; 100 мкг/г серы определено с коэффициентом вариации 5,2%. Если содержание серы меньше чем 5 мкг/г, следует отбирать пробы 1 г, а продолжительность определения 3 часа; 0,4 мкг/г серы определено с стандартной ошибкой 0,13 мкг/г. Точность метода в границах беспорядочных ошибок.

КОМПЛЕКСЫ ТЕТРАХЛОРГАЛЛАТА(III) С ОСНОВНИМИ ТРИФЕНИЛМЕТАНОВЫМИ И ДИФЕНИЛНАФТИЛМЕТАНОВЫМИ КРАСИТЕЛЯМИ:

V. ARMEANU and P. COSTINESCU, *Talanta*, 1967, **14**, 699.

Резюме—Приведен общий обзор свойств комплексов тетрахлоргаллата(III) с основними красителями трифенилметанометанового дифенилнафтилметанового классов; описываются также растворители для извлечения, спектри светопоглощения и молярные поглощения, оптимальные концентрации красителей и соляной кислоты, устойчивость соединений и их состав. Предложены аналитические методы определения следов галлия с использованием ряда етих комплексов.

ОПРЕДЕЛЕНИЕ ПРЕДЕЛА ЧУВСТВИТЕЛЬНОСТИ И ОПТИМАЛЬНЫХ АППАРАТУРНЫХ УСЛОВИЙ ДЛЯ ПРЕЦИЗИОННОЙ АБСОРБЦИОННОЙ СПЕКТРОФОТОМЕТРИИ ВЕЩЕСТВ В КОНДЕНСИРОВАННОЙ ФАЗЕ:

J. J. CETORELLI and J. D. WINEFORDNER, *Talanta*, 1967, **14**, 705.

Резюме—Получено выражение для отношения сигнала к фону в методе прецизионной абсорбционной спектрофотометрии молекул в конденсированной фазе и использовано для вычисления теоретического предела чувствительности и для предсказания оптимальных условий измерения на приборе. Рассматриваются одполучевие и двухлучевие приборы. Вычисленные теоретически значения C_{mt} для ряда органических молекул сравниваются с практически определенными пределными концентрациями C_{mp}, представляющими концентрации дающие светопоглощение 0,002. В случае интенсивного источника радиации и известного среднеквадратичного отклонения отношения сигнала к фоне надающей радиации в контрольном растворе, выражение для C_{mt} весьма простое и может применяться для каждого вещества с известным молярным светопоглощением. Изучено влияние параметров прибора на значение C_{mt}: обнаружено что только ширина щели монохроматора, число измерений сигнала пробы и стандарта, и ширина полосы ответа частоты электрометра имеют влияние на значение C_{mt} (для данной длины волны на монохроматоре).

Inorganic polarography in organic solvents—III. Analytical applications of metal–acetylacetonate complexes in toluene: B. K. AFGHAN, R. M. DAGNALL and K. C. THOMPSON, *Talanta*, 1967, **14**, 715 (Chemistry Department, Imperial College, London, S.W.7).

Summary—Indium and palladium are determined polarographically with a dropping mercury electrode in a toluene phase, following extraction as the acetylacetonates from aqueous solutions containing 2–10 ppm of the metals (or 0·1–0·5 ppm with a greater ratio of sample volume to solvent volume). Of 31 elements examined, only Co(III), Cr(III), Cu(II), Fe(III), In, Mo(VI), Pd and Ti(IV) gave extractable complexes with reduction waves in the available potential range. Specificity for palladium is obtained by extraction at pH 0·5, and for indium at pH 9 in the presence of cyanide and ascorbic acid as masking agents.

Determination of uranium in electro-refined plutonium by a combined ion-exchange and X-ray fluorescence technique: J. A. HAYDEN, *Talanta*, 1967, **14**, 721 (Analytical Development Group, Rocky Flats Division, Dow Chemical Company, P.O. Box 888, Golden, Colorado 80401, U.S.A.).

Summary—Uranium is separated from plutonium by adsorption on an anion-exchange resin from a concentrated hydrochloric acid solution and is eluted from the resin, collected on a disc of cation-exchange paper, and determined by X-ray fluorescence. The lower limit of detection is 2 μg of uranium, and 50 μg may be determined with a recovery of 98% and a standard deviation of 3·2 μg. In plutonium metal, 19 ppm of uranium were found, with a standard deviation of 2 ppm (6 results).

Spectrophotometric extractive titrations—IV. Determination of zinc in germanium dioxide and germanium chloride: AFTANAS GALÍK, *Talanta*, 1967, **14**, 731 (Lachema, N. C., Kaznějov, Plzeň-North, Czechoslovakia).

Summary—A simple and selective determination of zinc in germanium chloride and germanium dioxide is described. The sample is dissolved in sodium potassium tartrate solution and zinc is titrated spectrophotometrically at 532 mμ with a dithizone solution in carbon tetrachloride without discarding the organic phase. Interfering ions such as Bi(III), Cu(II), Cd(II), Co(II), Ni(II), Pb(II), Sn(II), Fe(II), Fe(III), Mn(II) and Tl(I) are masked with bis(2-hydroxyethyl)dithiocarbamate. The detection limit is $3{\cdot}23 \times 10^{-5}$% of zinc and this may be lowered by taking a larger sample and by performing the analysis in a closed system. A simplified technique, consisting of the simultaneous titration of the sample and blank, is described.

НЕОРГАНИЧЕСКАЯ ПОЛЯРОГРАФИЯ В ОРГАНИЧЕСКИХ РАСТВОРИТЕЛЯХ—III. ПРИМЕНЕНИЕ В АНАЛИЗЕ КОМПЛЕКСОВ МЕТАЛЛОВ С АЦЕТИЛАЦЕТОНОМ В ТОЛУОЛЕ:

B. K. Afghan, R. M. Dagnall and K. C. Thompson, *Talanta*, 1967, **14**, 715.

Резюме—Индий и палладий определяют полярографическим методом в растворе толуола с использованием капельного ртутного электрода, после экстрагирования комплексов с ацетилацетоном из водного раствора металлов, содержащего 2–10 мг/л металла (или 0,1–0,5 мл/л в случае большего отношения объема пробы и объема растворителя). Из исследованных 31 элементов только Co(III), Cr(III), Cu(II), Fe(III), In, Mo(VI), Pd и Ti(IV) дали экстрагируемые комплексы, имеющие волны восстановления в доступной области потенциала. Метод является избирательным для палладия если экстрагирование проводится при pH 0,5 ,а избирательным для индил при pH 9 в присутствии цианида и аскорбиновой кислоты в качестве маскирующих агентов.

ОПРЕДЕЛЕНИЕ УРАНА В ЭЛЕКТРООЧИЩЕННОМ ПЛУТОНИИ КОМБИНИРОВАННЫМ МЕТОДОМ ИОННОГО ОБМЕНА И ФЛУОРЕСЦЕНЦИИ РЕНТГЕНОВСКИХ ЛУЧЕЙ:

J. A. Hayden, *Talanta*, 1967, **14**, 721.

Резюме—Уран отделяют от плутония адсорбированием на анионообменной смоле из раствора в концентрированной соляной кислоте, элюируют из смолы, собирают на диске катионообменной бумаги и определяют методом флуоресценции рентгеновских лучей. Предел чувствительности 2 мкг урана, а 50 мкг можно определить с выходом 98% и стандартной ошибкой 3,2 мкг. В металлическом плутонии определено 19 мкг/г, с стандартной ошибкой 2 мкг/г (6 результатов).

ЭКСТРАКЦИОННО-СПЕКТРОФОТОМЕТРИЧЕСКИЕ ТИТРАЦИИ—IV. ОПРЕДЕЛЕНИЕ ЦИНКА В ДВУОКИСИ ГЕРМАНИЯ И ХЛОРИДЕ ГЕРМАНИЯ:

Aftanas Galík, *Talanta*, 1967, **14**, 731.

Резюме—Описан несложный и избирательный метод определения цинка в двуокиси и хлориде германия. Пробу растворяют в растворе виннокислого натрия-калия, а цинк титруют спектрофотометрическим методом при 532 ммк раствором дитизона в тетрахлорметане без отбрасывания органической фазы. Мешающие ионы как например Bi(III), Cu(II), Cd(II), Co(II), Ni(II), Pb(II), Sn(II), Fe(II), Fe(III), Mn(II) и Tl(I) маскируют бис(2-оксиэтил)дитиокарбаминатом. Предел определения цинка $3{,}23 \times 10^{-5}\%$ можно снижать взятием большей пробы и выполнением анализа в закрытой системе. Описана упрощенная процедура основывающаяся на одновременном титровании пробы и контрольного раствора.

Formation of mixed complexes in the extraction of indium with 1-(2-pyridylazo)-2-naphthol: YU. A. ZOLOTOV, I. V. SERYAKOVA and G. A. VOROBYEVA, *Talanta*, 1967, **14**, 737 (Vernadsky Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, Moscow, U.S.S.R.).

Summary—A detailed study has been made of the extraction of indium into chloroform by 1-(2-pyridylazo)-2-naphthol (PAN). The rate of extraction is maximal if the PAN is added to the aqueous phase and is not added as its chloroform solution. The ratio of indium to PAN is 1:1 and the cationic complex can be extracted only if a suitable anion is present, such as acetate or chloride.

Polarographic study of bis(2-pyridyl)disulphide di-*N*-oxide and bis(2-quinolyl)disulphide di-*N*-oxide in aqueous ethanol: I. EL-KHIAMI and R. M. JOHNSON, *Talanta*, 1967, **14**, 745 (Department of Chemistry, Chelsea College of Science and Technology, University of London, London, S.W.3).

Summary—The polarographic reduction of bis(2-pyridyl)- and of bis(2-quinolyl)disulphide di-*N*-oxide in aqueous alcohol yields aryl mercaptans. The electrode reaction is kinetically controlled by an initial one-electron transfer step, and values for the transfer coefficients and the specific heterogeneous rate constants for the forward reactions are presented. The polar *N*-oxide function in the α-position withdraws electrons from the disulphide bond, making the half-wave potential less negative than that of the diphenyl disulphide. The pK_a values of the mercapto compounds formed have been evaluated and the low values obtained for the heterocyclic *N*-oxides are further evidence for tautomerism in these compounds.

Instrumental activation analysis of vegetable tissue: E. STEINNES, *Talanta*, 1967, **14**, 753 (Isotope Laboratory, Institutt for Atomenergi, Kjeller, Norway).

Summary—A non-destructive method for the determination of bromine, manganese, phosphorus, potassium, sodium and zinc in plant tissue by neutron activation and gamma-ray spectrometry is described. Phosphorus and potassium have been determined also by beta-counting. The method should be especially attractive for analysis of manganese and zinc.

Some aspects of the reactions between selenium-containing ligands and platinum group metals: L. S. BARK and D. BRANDON, *Talanta*, 1967, **14**, 759 (Department of Chemistry and Applied Chemistry, University of Salford, Salford 5, U.K.).

Summary—2-(2-Pyridyl)benzo[*b*]selenophene has been investigated as a possible reagent for palladium. From a consideration of its reactions with diverse metal ions, and the probable structure of the complex formed between the compound and palladium(II) it is postulated that the group —Se···C···C···N— may be highly selective for palladium. From the experimental evidence it is suggested that the delocalization of the metal electron density by π-bond formation between the palladium and selenium atoms is a major factor in determining the stability of the chelated complex.

ОБРАЗОВАНИЕ СМЕШАННЫХ КОМПЛЕКСОВ ПРИ ЭКСТРАГИРОВАНИИ ИНДИЯ 1-(2-ПИРИДИЛАЗО)-2-НАФТОЛОМ:

Yu. A. Zolotov, I. V. Seryakova and G. A. Vorobyeva, *Talanta*, 1967, **14**, 737.

Резюме—Подробно изучено экстрагирование в хлороформ индия 1-(2-пиридилазо)-2-нафтолом (ПАН). Скорость экстрагирования максимальная, если ПАН добавляют водной фазе, а не в форме раствора в хлороформе. Отношение индия и ПАН 1:1, ц катионный комплекс экстрагируется только в присутствии подходящего аниона, как например ацетата или хлорида.

ПОЛЯРОГРАФИЧЕСКОЕ ИЗУЧЕНИЕ ДИ-*N*-ОКИСИ БИС(2-ПИРИДИЛ) ДИСУЛЬФИДА И ДИ-*N*-ОКИСИ БИС(2-ХИНОЛИЛ)ДИСУЛЬФИДА В ВОДНОМ РАСТВОРЕ ЭТИЛОВОГО СПИРТА:

I. El-Khami and R. M. Johnson, *Talanta*, 1967, **14**, 745.

Резюме—При полярографическом восстановлении ди-*N*-окисей бис(2-пиридил) дисульфида и бис(2-хинолил)дисульфида образуются арилмеркаптаны. Электродная реакция регулирована кинетически начальным переходом одного электрона; приведены величины коэффициента переноса и констант скорости гетерогенной реакции. Полярная функциональная группа *N*-окиси в положении альфа отнимает электроны из полосы дисульфида, в результате чего потенциал этой полуволны является менее отрицательным чем полуволны дифенилдисульфида. Определены величины pK_a образующихся меркаптосоединений: полученные для гетероциклических *N*-окисей визкие величины также свидетельствуют о таутомерии в этих соединениях.

ИНСТРУМЕНТАЛЬНЫЙ АКТИВАЦИОННЫЙ АНАЛИЗ РАСТИТЕЛЬНОЙ ТКАНИ:

E. Steinnes, *Talanta*, 1967, **14**, 753.

Резюме—Описан недеструктивный метод определения брома, марганца, фосфора, калия, натрия и цинка в растительной ткани, основывающийся на нейтронноактивационном анализе и спектрометрии гамма лучей. Фосфор и калий определялы также путем считания бета-частиц. Метод является особенно подходящим для анализа марганца и цинка.

НЕКОТОРЫЕ ВИДЫ РЕАЦИЙ МЕЖДУ СОДЕРЖАЮЩИМИ СЕЛКН ЛИГАНДАМИ И МЕТАЛЛАМИ ПЛАТИНОВОЙ ГЕРУППЫ:

L. S. Bark and D. Brandon, *Talanta*, 1967, **14**, 759.

Резюме—2-(2-Пиридил)бензо(*b*)селенофен был изучен в качестве реагента для палладия. На основании реакций этого реагента с различными ионами металлов и предполагаемого строения комплекса образующегося между реагентом и палладием(II) авторы считают группу —Se···C···C··· И—высокоизбирательной для палладия. На основании экспериментальных данных предложено, что делокализация плотности электронов металла образованием π-связи между атомами палладия и селена представляет собой главный фактор при определении устойчивости комплекса.

Kinetics of the precipitation of palladium dimethylglyoximate from homogeneous solution: PAUL R. ELLEFSEN and LOUIS GORDON, *Talanta*, 1967, **14**, 769 (Department of Chemistry, Case Institute of Technology, Cleveland, Ohio, U.S.A.).

Summary—The kinetics of formation of palladium dimethylglyoximate in the post-nucleation and pre-nucleation stages, and the effect of palladium on the reaction of biacetyl and hydroxylamine, have been studied.

Mass spectrometry of metal chelates—I. Detection on the picogram scale: A. E. JENKINS and J. R. MAJER, *Talanta*, 1967, **14**, 777 (Department of Chemistry, P.O. Box 363, The University, Birmingham, 15, U.K.).

Summary—A method has been developed for the detection and estimation of metals in the form of chelates in amounts down to 10^{-12} g. The chelate is evaporated into the source of a mass spectrometer and a continuous record of the ion current at a significant mass number is made. The integrated ion current is directly proportional to the concentration of metal chelate.

Anion-exchange separation of cobalt from nickel: O. G. BALAKRISHNAN NAMBIAR and P. R. SUBBARAMAN, *Talanta*, 1967, **14**, 785 (National Chemical Laboratory, Poona-8, India).

Summary—An anion-exchange method has been developed for the separation of cobalt from nickel, based on the observation that from a malonic acid solution containing sodium nitrite, cobalt is preferentially adsorbed by the exchanger but nickel passes through. The cobalt is eluted with 2*M* ammonium chloride in dilute ammonia solution. From an ammonium malonate solution containing chloride and nitrate, cobalt is quantitatively electro-deposited on a platinum cathode to give a bright, adherent deposit. Nickel is deposited from a solution of similar composition.

Emission spectra of nitrous oxide supported acetylene flames at atmospheric pressure: G. F. KIRKBRIGHT, M. K. PETERS and T. S. WEST, *Talanta*, 1967, **14**, 789 (Chemistry Department, Imperial College, London, S.W.7).

Summary—The emission spectra of a premixed flame of acetylene supported by nitrous oxide have been recorded under different fuel-gas mixture conditions. The emission spectra in these flames of a series of metals, for which it is difficult to obtain a significant population of ground state atoms for atomic absorption spectroscopy in more conventional flames, have also been studied. The red secondary zone which is present in the fuel-rich flames shows emission attributable to long-lived CN and NH species which form a strongly reducing atmosphere to inhibit refractory oxide formation from elements such as molybdenum, titanium and aluminium introduced into the flame. An attempt has also been made to explain some of the reactions which may occur between the flame species above the primary reaction zone.

КИНЕТИКА ОСАЖДЕНИЯ ДИМЕТИЛГЛИОКСИМАТА ПАЛЛАДИЯ ИЗ ГОМОГЕННОГО РАСТВОРА:

PAUL R. ELLEFSEN and LOUIS GORDON, *Talanta*, 1967, **14**, 769.

Резюме—Изучена кинетика образования диметилглиоксимата палладия в фазах после и пред образованием центров кристаллизации, и влияние палладия на реакцию диацетила с гидроксиламином.

МАСС-СПЕКТРОМЕТРИЯ ХЕЛАТОВ МЕТАЛЛОВ—I. ОТКРЫТИЕ ПИКОГРАММОВЫХ КОЛИЧЕСТВ:

A. E. JENKINS and J. R. MAJER, *Talanta*, 1967, **14**, 777.

Резюме—Разработан метод открытия и определения количеств металлов в форме их хелатов все до 10^{-12} г. Хелат испаривают в камеру масс-спектрометра и получают непрерывный запись ионного тока при знаменательном массовом числе. Интегрированный ионный ток прямо пропорционален концентрации хелата металла.

ОТДЕЛЕНИЕ КОБАЛЬТА ОТ НИКЕЛЯ МЕТОДОМ АНИОННОГО ОБМЕНА:

O. G. BALAKRISHNAN NAMBIAR and P. R. SUBBARAMAN, *Talanta*, 1967, **14**, 785.

Резюме—Разработан метод анионного обмена для отделения кобальта от никеля, основывающийся на наблюдении что из содержающего нитрит натрия малоновокислого раствора кобальт адсорбируется на ионообменнике в то время как никель не адсорбируется. Кобальт елюируют 2*M* хлоридом аммония в разбавленном аммиачном растворе. Из раствора малоната аммония, содержающего хлорид-и нитратионы, кобальт электроосаждается количественно на платиновом катоде, образуя блестящий, плотно пристающий к основе осадок. Никель осаждается из растовра подобного состава.

ЭМИССИОННЫЕ СПЕКТРИ СОДЕРЖАЩИХ ЗАКИСЬ АЗОТА ПЛАМЁН АЦЕТИЛЕНА ПРИ АТМОСФЕРНОМ ДАВЛЕНИИ:

G. F. KIRKBRIGHT, M. K. PETERS and T. S. WEST, *Talanta*, 1967, **14**, 789.

Резюме—Эмиссионные спектры предварительно смешанного пламени ацетилена и закиси азота записаны для различных отношений компонентов в смеси. Также были изучены эмиссионные спектры ряда металлов в этих пламенах, для которых трудно получить довольное число атомов в основном состоянии для атомно-абсорбционной спектрофотометрии в более обыкновенных пламенах. Красная вторичная зона, присутствующая в пламенах с высоким содержанием топлива показывает эмиссию, которую можно приписать группам долгой жизни CN и NH, образующим сильно восстанавливающую атмосферу что бы препятствовать образование огнестойких окисей из внесепных в пламя элементов, на пример молибдена, титана и алюминия. Авторы также пытались объяснить некоторые реакции, появляющиеся в пламени над первичной зоной.

Concentration and separation of indium, gallium, thallium, antimony and bismuth by extraction with alkylphosphoric acids: I. S. LEVIN, A. A. SHATALOVA, T. G. AZARENKO, I. A. VORSINA, N. A. BURTOVAYA-BALAKIREVA and T. F. RODINA, *Talanta*, 1967, **14**, 801 (Institute of Mineral Treatment, Derzhavina 18, Novosibirsk, U.S.S.R.).

Summary—The use of alkylphosphoric acids for solvent extraction separations is described, and the use of antisynergic agents for stripping is discussed.

APDC–MIBK extraction system for the determination of trace elements in saline waters by atomic-absorption spectrophotometry: ROBERT R. BROOKS, BOB J. PRESLEY and ISAAC R. KAPLAN, *Talanta*, 1967, **14**, 809 (Department of Geology and Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California, U.S.A.).

Summary—A technique has been developed for the determination of "soluble" cobalt, copper, iron, lead, nickel and zinc in saline waters by simultaneous extraction of their complexes with ammonium pyrollidine dithiocarbamate (APDC) into methyl isobutyl ketone (MIBK) and subsequent analysis by atomic-absorption spectrophotometry. Particulate matter is analysed separately by dissolving millipore filters in an acetone–hydrochloric acid mixture. Various analytical and instrumental parameters have been evaluated. The method is self-compensating in that it makes allowance for any incomplete extraction of the complexes. The technique has been applied to the determination of these elements in sea-water and saline lakes.

Radiochemical separations by the ring-oven method—II: The system ^{99}Mo/^{99m}Tc: D. KLOCKOW, *Talanta*, 1967, **14**, 817 (Chemistry Laboratory, The University, Freiburg i. Br., Germany).

Summary—The separation of ^{99}Mo and ^{99m}Tc by the ring-oven technique is described. The separation is best carried out on round papers impregnated with Prussian Blue or with manganese dioxide, when the molybdenum is fixed in the centre of the paper and the technetium is concentrated with 70–90% yield in the ring. Decontamination factors of $\geqslant 10^3$ were obtained. ^{99m}Tc formed after the separation can be further leached from the parent nuclide. The half-life of ^{99m}Tc was found to be 6·06 $\pm$ 0·05 hr.

КОНЦЕНТРИРОВАНИЕ И РАЗДЕЛЕНИЕ ИНДИЯ, ГАЛЛИЯ, ТАЛЛИЯ, СУРЬМЫ И ВИСМУТА ИЗВЛЕЧЕНИЕМ АЛКИЛФОСФОРНЫМИ КИСЛОТАМИ:

I. S. Levin, A. A. Shatalova, T. G. Azarenko, I. A. Vorsina, N. A. Burtova-Balakireva and T. F. Rodina, *Talanta*, 1967, **14**, 801.

Резюме—Обсуждается применение алкилфосфорных кислот в разделениях основывающихся на извлечении растворителями, и использование антисинергетических агентов для реэкстракцим.

СИСТЕМА ЭКСТРАКЦИИ АПДК–МИБК ДЛЯ ОПРЕДЕЛЕНИЯ СЛЕДОВЫХ ЭЛЕМЕНТОВ В СОЛЕНЫХ ВОДАХ МЕТОДОМ АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОФОТОМЕТРИИ:

Robert R. Brooks, Bob J. Presley and Isaac R. Kaplan, *Talanta*, 1967, **14**, 809.

Резюме—Разработана процедура для определения «растворимого» кобальта, меди, железа, свинца, никеля и цинка в соленых водах одновременным экстрагированием их комплексов с пирролидиндитиокарбаминатом аммония (АПДК) метилизобутилкетоном (МИБК) и последовательным анализом методом атомно-абсорбционной спектрофотометрии. Частицы анализируют отдельно, растворением миллипорфильтров в смеси ацетона и соляной кислоты. Испытаны различные аналитические и аппаратные параметры. Метод самокомпенсирующий, потому что принимает во внимание неполную экстракцию комплексов. Процедурой пользовались для определения этих элементов в морской воде и соленых озерах.

РАДИОХИМИЧЕСКИЕ ВЫДЕЛЕНИЯ С ИСПОЛЬЗОВАНИЕМ КОЛЬЦЕВОЙ ПЕЧИ—II: СИСТЕМА ^{99}Mo/^{99m}Tc:

D. Klockow, *Talanta*, 1967, **14**, 817.

Резюме—Описано разделение ^{99}Mo и ^{99m}Tc методом кольцевой печи. Разделение лучше всего проводится на круглых бумажных дисках пропитанных берлинской лазурью или двуокисью марганца: молибден адсорбируется в центре диска, а технеций концентрируется в кольце с выходом 70–90%. Получены факторы деконтаминации $>10^3$. Образованный после разделения ^{99m}Tc можно элюировать от маточного нуклида. Полупериод ^{99m}Tc равен 6,06 ± 0,05 часов.

Determination of traces of calcium, magnesium, iron and nickel in aluminium salts by atomic-absorption spectrophotometry with a microwave-excited source and hollow-cathode lamps: G. B. MARSHALL and T. S. WEST, *Talanta*, 1967, **14**, 823 (Chemistry Department, Imperial College, London, S.W.7).

Summary—The determination of trace amounts of calcium and magnesium in solutions containing large concentrations of aluminium salts may be accomplished by co-precipitating their hydroxides on iron(III) hydroxide, dissolving the precipitate, and extracting the 8-hydroxyquinolates of calcium and magnesium into methyl isobutyl ketone at about pH 11. The extract may be sprayed into the air-propane flame of a simple unmodulated spectrophotometer and atomic-absorption measurements for calcium and magnesium made at 4227 and 2852 Å respectively. The limits of determination correspond to 10 and 1 ppm of calcium and magnesium in solid alumina. Iron and nickel may be co-precipitated on hydrated manganese(IV) oxide and their 8-hydroxyquinolates extracted at pH 4·5. Measurements of atomic absorption for these elements at 2483 and 2320 Å respectively yield limits of determination corresponding to 10 ppm in alumina. Hollow-cathode lamps may be used for calcium, magnesium and nickel, but a simple microwave-excited discharge tube gives much better sensitivity than a hollow-cathode lamp for iron.

Computer calculation of equilibrium concentrations in mixtures of metal ions and complexing species: D. D. PERRIN and I. G. SAYCE, *Talanta*, 1967, **14**, 833 (Department of Medical Chemistry, Australian National University, Canberra, Australia).

Summary—A method is described for calculating equilibrium concentrations of all species in multi-metal—multi-ligand mixtures from the pH of the solution, the total concentration of each metal and each complexing agent, and the relevant equilibrium constants (pK_a values and stability constants). No restriction is imposed on types of possible complexes, which can include mixed, hydrolysed, protonated and polynuclear species. Two examples are given. One of these comprises a 10-metal–10-ligand system (195 equilibrium constants). In the second system, mixed complex formation is important. The computer program is given.

End-point sharpness in thermometric titrimetry: H. J. V. TYRRELL, *Talanta*, 1967, **14**, 843 (Department of Chemistry, Chelsea College of Science and Technology, Manresa Road, London, S.W.3).

Summary—It is shown that the sharpness of an end-point in a thermometric titration where the simple reaction

$$A + B \rightleftharpoons AB$$

takes place, depends on Kc_A' where K is the equilibrium constant for the reaction, and c_A' is the total concentration of the titrand (A) in the reaction mixture. The end-point is sharp if, (*i*) the enthalpy change in the reaction is not negligible, and (*ii*) $Kc_A' > 10^3$. This shows that it should, for example, be possible to titrate 0·1*M* acid, $pK_A = 10$, using a thermometric end-point. Some aspects of thermometric titrimetry when $Kc_A' < 10^3$ are also considered.

ОПРЕДЕЛЕНИЕ СЛЕДОВ КАЛЬЦИЯ, МАГНИЯ, ЖЕЛЕЗА И НИКЕЛЯ В СОЛЯХ АЛЮМИНИЯ МЕТОДОМ АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОФОТОМЕТРИИ С ИСПОЛЬЗОВАНИЕМ ВОЗБУЖДЕННОГО МИКРОВОЛНАМИ ИСТОЧНИКАИЛАМПС ПОЛЫМ КАТОДОМ:

G. B. Marshall and T. S. West, *Talanta*, 1967, **14**, 823.

Резюме—Определение следовых количеств кальция и магния в содержащих большие колвчества солей алюминия растворах осуществлено соосаждением их гидроокисей на гидроокиси железа(III), растворением осадка и экстрагированием 8-оксихинолинатов кальция и магния метилизобутилкетоном при pH II. Экстракт вводится в пламя пропана и воздуха простого вемодулированного спектрофотометра и измеряется атомное поглощение кальция и магния при 4227 и 2852 Å, соответсвенно. Предел определения в твердой окиси алюминия 10 мкг/г кальция и 1 мкг/г магния. Железо и никель соосаждаются на гидроокиси марганца(IV), а их 8-оксихинолинаты экстрагируются при pH 4,5. Измерение атомного поглощения этих элементов при 2483 и 2320 Å дает предел определения 10 мкт/г в окиси алюминия. Лампы с полым катодом пригодны для определения кальция, магния и никеля, но простой возбужденной микроволнами разрадной лампой получается значительно лучшая чувствительность для железа чем лампой с полым катодом.

ИСПОЛЬЗОВАНИЕ ЭЛЕКТРОННОВЫЧИСЛИТЕЛЯ ДЛЯ ВЫЧИСЛЕНИЯ РАВНОВЕСНЫХ КОНЦЕНТРАЦИЙ В СМЕСЯХ ИОНОВ МЕТАЛЛОВ И КОМПЛЕКСООБРАЗОВАТЕЛЕЙ:

D. D. Perrin and I. G. Sayce, *Talanta*, 1967, **14**, 833.

Резюме—Описан метод вычисления равновесных концентраций всех компонентов в содержащих ряд металлов и лигандов системах, па основе pH раствора, общей концентрации каждого металла и каждого лиганда и уместных констант равповесия (величин pK_a и констант устойчивости). Метод не ограничивается на известные типы комплексов, они могут включать смешанные, гидролизированные, протонованные и многоядерные комплексы. Приведены два примера. Один из них представляет систему 10 металлов и 10 лигандов (195 констант равновесня). В другой системе значительно образование смешанных комплексов. Сообщена программа для электронновычислительного прибора.

ОСТРОТА КОНЦА ТИТРОВАНИЯ В ТЕРМОМЕТРИЧЕСКОЙ ТИТРИМЕТРИИ:

H. J. V. Tyrrell, *Talanta*, 1967, **14**, 843.

Резюме—Показано что острота конца титрования при термометрической титрации, представленной простим уравнением

$$A + B \rightleftharpoons AB$$

зависит от Kc_A', где K константа равновесия реакции, а c_A' суммарная концентрация титранда (A) в реакционной смеси. Конец титрования острый, если (1) перемена энтальпии реакции значительна, а (2) $Kc_A' > 10^3$. На основании этого, на пример, можно титровать 0,1M раствор кислоты, $pK_A = 10$, с использованием термометрического конца титрования. Рассмотрены некоторые взгляды на термометрическую титрацию в случае $Kc_A' < 10^3$.

Oxidimetric determination of indigo with iron(III) and hexacyanoferrate-(III): G. GOPALA RAO and V. RUKMINI, *Talanta*, 1967, **14**, 849 (Andhra University, Waltair, India).

Summary—The use of iron(III) in sulphuric acid medium and of potassium hexacyanoferrate(III) in hydrochloric acid medium has been investigated for the oxidimetric determination of indigo and indigo sulphonic acid. Conditions have been established for the assay of the dye with iron(III) sulphate at 100° and with potassium hexacyanoferrate-(III) at room temperature.

Milligram determination of aromatic amines and phenols with *N*-bromosuccinimide: R. D. TIWARI, J. P. SHARMA and I. C. SHUKLA, *Talanta*, 1967, **14**, 853 (Department of Chemistry, University of Allahabad, Allahabad, India).

Summary—A simple and rapid method has been developed for the determination of milligram amounts of aromatic amines and phenols. An aliquot containing 2–4 mg of sample is dissolved in a mixture of hydrochloric and acetic acids and allowed to react with *N*-bromosuccinimide, the excess of which is determined iodometrically after the reaction is over. The reaction time varies from 1–10 min and the absolute error generally is negative, ranging from −1 to −4%.

Microchemical detection of isocyanides: E. V. CRABTREE, E. J. POZIOMEK and D. J. HOY, *Talanta*, 1967, **14**, 857 (Physical Research Laboratory, Edgewood Arsenal, Maryland 21010, U.S.A.).

Summary—Microgram quantities of isocyanides may be easily detected on filter paper or in tubes of silica gel by using benzidine acetate–copper(II) acetate or *p,p'*-tetramethyldiaminodiphenylmethane–copper(II) sulphate reagents. Interferences include those substances which are known to interfere in the use of the same reagents for the detection of hydrogen cyanide. The lowest amount of n-, s-, or t-butyl isocyanide detectable is approximately 0·1 μg.

***p*-Aminoacetophenone as a reagent for the colorimetric determination of cerium(IV):** G. SOMIDEVAMMA and M. S. SARMA, *Talanta*, 1967, **14**, 861 (Department of Chemistry, Andhra University Colleges, Waltair, India).

Summary—With a solution of *p*-aminoacetophenone, cerium(IV) gives a purple colour which can be used for its detection and determination. The limits of identification and dilution are 1·0 μg and 1 in 50000 respectively. Beer's law is obeyed in the range 14–350 μg. The colour is stable for only 5 min and measurements of absorbance must be made quickly. The interferences are fewer than with existing methods.

ОКСИДИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ИНДИГО ЖЕЛЕЗОМ(III) И ГЕКСАЦИАНОФЕРРАТОМ(III):

G. Gopala Rao and V. Rukmini, *Talanta*, 1967, **14**, 849.

Резюме—Изучено использование железа(III) в сернокислой среде и гексацианоферрата(III) калия в солянокислой среде для оксидиметрического определения индиго и индигосульфокислоты. Установлены условия для анализа красителя сульфатом железа(III) при 100° и гексацианоферратом(III) калия при комнатной температуре.

ОПРЕДЕЛЕНИЕ АРОМАТИЧЕСКИХ АМИНОВ И ФЕНОЛОВ НА МИЛИГРАММОВОЙ ШКАЛЕ *N*-БРОМСУКЦИНИМИДОМ:

R. D. Tiwari, J. P. Sharma and I. C. Shukla, *Talanta*, 1967, **14**, 853.

Резюме—Разработан быстрый и несложный метод определения миллиграммовых количеств ароматических аминов и фенолов. Аликвотную часть, представляющую 2-4 мг пробы растворяют в смеси соляной и уксусной кислот и реагируют с N-бромсукцинимидом, избыток которого определяют иодометрическим методом после окончания реакции. Продолжительность реакции 1–10 мин, а абсолютная ошибка в большинстве случаев отрицательная, колеблющаяся от −1 до −4%.

МИКРОХИМИЧЕСКОЕ ОБНАРУЖЕНИЕ ИЗОНИТРИЛОВ:

E. V. Crabtree, E. J. Poziomek and D. J. Hoy, *Talanta*, 1967, **14**, 857.

Резюме—Микрограммовые количества изонитрилов могут обнаружится на фильтровальной бумаге или трубках силикагеля смесью ацетата бензидина и ацетата меди(II) или смесью п,п'-тетраметилдиаминодифенилметана и сульфата меди(II) в качестве реагентов. Определению мешают вещества, влияющие на определение цианистого водорода теми же реагентами. Метод позволяет обнаружение до 0,1 мкг н-, с- или н-бутилизонитрила.

П-АМИНОАЦЕТОФЕНОН КАК РЕАГЕНТ ДЛЯ КОЛОРИМЕТРИЧЕСКОГО ОПРЕДЕЛЕНИЯ ЦЕРИЯ(IV):

G. Somidevamma, and M. S. Sarma, *Talanta* 1967, **14**, 861.

Резюме—С раствором п-аминоацетофенона церий(IV) дает пурпурную окраску которой можно пользоваться для его обнаружения и определения. Пределы отождествления и разбавления 1,0 мкг и 1 в 50,000, соответственно. Закон Бера соблюдается в пределах 14–350 мкг. Окраска устойчивая только в течение 5 мин., потому измерение светопоглощения следует проводить быстро. Описанный метод меньше подлежает влиянию других ионов чем обыкновенные методы.

Some solvent effects on the solvent extraction of 8-quinolinol: HORACIO A. MOTTOLA and HENRY FREISER, *Talanta*, 1967, **14**, 864 (Department of Chemistry, University of Arizona, Tucson, Arizona 85721, U.S.A.).

Summary—The distribution constants of 8-quinolinol between water and a series of substituted aliphatic hydrocarbons, at 25°, are reported. The results are discussed in terms of dielectric constant and solubility parameter of the solvents. For 8-quinolinol, and possibly for its chelates, bromochloromethane, dibromomethane and chloroform seem to be about the best solvents, in that order. Among the solvents studied, chloroform shows significantly higher values than expected; the deviation may be explained by a specific interaction of the hydrogen-bonding type.

Explosion hazards with xenon trioxide solutions ("xenic acid"): JOHN H. HOLLOWAY, *Talanta*, 1967, **14**, 871 (Department of Chemistry, University of Aberdeen, Old Aberdeen, Scotland).

Summary—Attention is drawn to the explosion hazards associated with xenic acid (xenon trioxide solution) and hence all xenon compounds that can yield xenon trioxide by hydrolysis.

Spectrophotometric determination of chromium with Xylenol Orange and Methylthymol Blue: K. L. CHENG, *Talanta*, 1967, **14**, 875 (Department of Chemistry, University of Missouri at Kansas City, Kansas City, Missouri 64110, U.S.A.).

Summary—A new simple and sensitive method for determining traces of chromium is described. Xylenol Orange and chromium(III) form a red complex at pH 3 on heating in boiling water for 20 min. The molar absorptivity is $19{\cdot}0 \times 10^3$. No catalytic action of the bicarbonate ion, carbon dioxide, or chromium(II) generated by metallic zinc was observed. Methylthymol Blue is a less sensitive reagent for chromium, the molar absorptivity being $11{\cdot}5 \times 10^3$.

Solvent extraction of ammine complexes: M. KYRŠ and M. PIVOŇKOVÁ, *Talanta*, 1967, **14**, 877 (Nuclear Research Institute, Czechoslovak Academy of Sciences, Řež near Prague, Czechoslovakia).

Summary—The ammine complexes of zinc and of cobalt(II) can be extracted effectively as the dipicrylaminates or tetraphenylborates by using nitrobenzene as the solvent.

ВЛИЯНИЕ РАСТВОРИТЕЛЯ В ЭКСТРАКЦИИ РАСТВОРИТЕЛЯМИ 8-ХИНОЛИНОЛА:

HORACIO A. MOTTOLA and HENRY FREISER, *Talanta*, 1967, **14**, 864.

Резюме—Определены константы распределения 8-хинолинола между водой и рядом замещенных алифатических углеводородов при 25°. Результаты обсуждены ссиляясь на диэлектрическую постоянную и параметр растворимости растворителей. Для 8-хинолинола и—возможно—для его хелатов бромохлорметан, дибромметан и хлороформ представляют собой найуспешные растворители, в том же порядке. От исследованных растворителей, хлороформом получаются значителńо больше величины от ожиданых; эту неправильность можно объяспить на основе специфического взаймодейсвия типа водородной связи.

ОПАСНОСТЬ ВЗРЫВА РАСТВОРОВ ТРЁХОКИСИ КСЕНОНА ("КСЕНОНОВОЙ КИСЛОТЫ"):

JOHN H. HOLLOWAY, *Talanta*, 1967, **14**, 871.

Резюме—Обращастся внимание на опасность взрыва, связанную с ксеноновой кислотой (раствором трёхокиси ксенона) и со всеми соединениями ксепона, дающими трёхокис ксенона путем гидролиза.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ХРОМА КСИЛЕНОЛОРАНЖЕВЫМ И МЕТИЛТИМОЛСИНИМ:

K. L. CHENG, *Talanta*, 1967, **14**, 875.

Резюме—Описан новый несложный и чувствительный метод определения следов хрома. Ксиленолоранжевый образует с хромом(III) красный комплекс при pH 3, нагреванием в кипящей воде через 20 мин. Не обпаружено каталитическое действие бикарбонатиона, двуокиси углерода или хрома(II), генерированных металлическим цинком. Метилтимолсиний является менее чувствительным реагентом на хром, дающий молярное поглощение $11{,}5 \times 10^3$.

ЭКСТРАКЦИЯ РАСТВОРИТЕЛЯМИ АММИНОВЫХ КОМПЛЕКСОВ:

M. KYRŠ and M. PIVOŇKOVÁ, *Talanta*, 1967, **14**, 877.

Резюме—Амминовые комплексы цинка и кобальта(II) успешно экстрагируются нитробензолом в качестве растворителя в форме дипикриламинатов или тетрафенилборатов.

Talanta, 1967, Vol. 14, p. iv. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

PRAGUE

3–17 *September* 1967, **VI Internationaler Polarographischer Kursur.**

Dieser Kursus besteht aus Vorlesungen über die Grundlagen der Polarographie und Oszillopolarographie, und einem entsprechendem Praktikum. Der Lehrgang ist für Hochschulabsolventen gedacht, jedoch sind eingehende Kenntnisse der Polarographie nicht Vorbedingung. Die Zahl der Teilnehmer wurde auf 40 Personen begrenzt. Die Teilnehmer werden in zwei Gruppen eingeteilt. Die Vorlesungen und das Praktikum werden in deutscher Sprache abgehalten, aber falls eine ausreichende Anzahl der Teilnehmer es vorziehen sollte, wird die englische Sprache für eine der beiden Gruppen verwendet werden.

Der Lehrgang wurde unter Aufsicht des Herrn Professor Dr. J. Heyrovský zusammengestellt. Die Vorlesungen und das Praktikum werden von wissenschaftlichen Fachkräften der Karlsuniversität und des J. Heyrovský Polarographischen Institutes gehalten, resp. geleitet werden (Doz. J. Kůta, Prof. A. Vlček, Prof. P. Zuman und andere). Die Teilnahmegebühr beträgt Kčs 600,– –, einschliesslich der Kosten eines Ausfluges in die Umgebung von Prag und eines gemeinsamen Abendessens am letzten Tage des Lehrganges. Alle Teilnehmer erhalten eine vervielfältigte Anleitung zu den Laboratoriumsversuchen. Unterbringung in Studentenheimen zu mässigen Preisen wird gewährleistet.

Die Anmeldungen sind an das Institut für Physikalische Chemie der Karlsuniversität, Prag 2, Albertov 2030, Dozent V. Kalous, bis spätestens Ende Juni 1967 zu richten.

U.S.A.

14–18 *August* 1967, **Gordon Research Conference on Analytical Chemistry,** New Hampton School, New Hampton, New Hampshire. Chairman; C. W. Zuehlke; Vice Chairman; D. N. Hume. For further information write to: W. George Parks, Director University of Rhode Island Kingston, Rhode Island, U.S.A.

5–9 *September* 1967, **22nd annual Molecular Spectroscopy Symposium,** Columbus Ohio.

In addition to our usual programme of Invited Speakers and Contributed Papers, we will have three specially arranged seminars on Rapid Scanning Spectroscopy, Far Infrared Problems, and New Experiments with Molecular Beams. For further information write to: K. Narahari Rao, The Ohio State University, Dept. of Physics, 174 West 18th Avenue, Columbus, Ohio 43210, U.S.A.

10–12 *October* 1967, **Eleventh Conference on Analytical Chemistry in Nuclear Technology,** Mountain View Hotel, Gatlinburg, Tennessee sponsored by the Analytical Chemistry Division, Oak Ridge National Laboratory.

The theme of this years conference is "Instrumental Methods in Analytical Chemistry". Papers, up to 25 min in length, dealing with instrumentation and instrumental applications in areas such as radiochemistry electrochemistry, spectrophotometry, spectroscopy, chromatography, automated methods of analysis, and chemical separations, are solicited by the committee. Special symposia will be arranged by the committee as interest dictates.

Talanta, 1967, Vol. 14, p. iv. Pergamon Press Ltd. Printed in Northern Ireland

PUBLISHER'S ANNOUNCEMENT

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"Applications of Nuclear and Electron Magnetic Resonance in Analytical Chemistry" by B. D. Flockhart and R. C. Pink.

"A Critical Evaluation of Colorimetric Methods for Determination of Noble Metals—III. Palladium and Platinum" by F. E. Beamish.

"A Critical Evaluation of Colorimetric Methods for Determination of the Noble Metals—III. Rhodium, Iridium, Ruthenium, Osmium and Gold" by F. E. Beamish.

"Present State of Complexometry—I. Determination of Quadrivalent and Tervalent Metals" by Rudolf Přibil.

"Some Recent Developments in Radioactivation Analysis: A Review of Improvements in the Analytical Technique" by F. Girardi.

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"A Critical Review of Gravimetric Methods for Determination of the Noble Metals—II" by F. E. Beamish.

"A Critical Review of Titrimetric Methods for Determination of the Noble Metals—II" by F. E. Beamish.

"Present State of Complexometry—II. Determination of Bivalent Metals" by Rudolf Přibil.

"Derivatography: A Complex Method in Thermal Analysis" by F. Paulik, J. Paulik and L. Erdey.

"Potassium Dichromate as an Oxidimetric Reagent" by G. Gopala Rao.

"Newer Acylation Methods for the Determination of Organic Hydroxyl and Amino Compounds" by N. K. Mathur.

"A Critical Review of Neutron Activation and Tracer Methods for the Determination of the Noble Metals" by F. E. Beamish, K. S. Chung and A. Chow.

COPIES OF HONOUR ISSUES

Single copies of the following Honour Issues of Talanta are available from Subscriptions Department, Pergamon Press Ltd. Headington Hill Hall, Oxford, England, or Pergamon Press Inc., 44-01 21st Street, Long Island City, New York 11101, USA., at £2 or $6.50 per copy:

Willard Honour Issue	February 1961	**Kolthoff Honour Issue**	February 1964
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	Smith Honour Issue	July 1966	

SUMMARIES FOR CARD INDEXES

Countercurrent Ionophoresis—II. Practical Applications: W. PREETZ and H. L. PFEIFER, *Talanta*, 1967, **14**, 143 (Institute for Analytical Chemistry and Radiochemistry, University of Saarland, Saarbrücken, Germany).

Summary—By use of a new apparatus it has been possible to confirm the principle and course of countercurrent ionophoresis, by applying it to model anionic substances. Qualitative investigation showed that the anions were arranged between the anode and cathode according to their mobilities. For the formation of a stationary state the anions in the anode and countercurrent electrolytes must have greater mobility, and the anions of the effluent and cathode electrolytes a lower mobility, than the anions in the mixture to be separated. Field intensity measurements in a chamber with a capillary separation gap show that there is a sharpe change in the field intensity at the boundaries of the stationary zones, and this intensity profile is responsible for the sharp separations obtained. By comparison of field intensity factors and known mobilities it is possible to calculate other ionic mobilities. The concentrations of ions in the zones can be calculated from the ionic mobilities and the concentration of the countercurrent solution.

Cation-exchange behaviour of several elements in hydrochloric acid—organic solvent media: J. KORKISCH and S. S. AHLUWALIA, *Talanta*, 1967, **14**, 155 (Analytical Institute, University of Vienna IX, Währingerstrasse 38, Austria).

Summary—In the present paper the cation-exchange characteristics of 20 elements towards the strongly acidic cation-exchange resin Dowex 50X8 in media containing varying concentrations of organic solvents and aqueous hydrochloric acid were investigated. Based on the determination of the distribution coefficients of these elements in the organic solvents methanol, ethanol, n-propanol, isopropanol, methyl glycol, acetone, tetrahydrofuran and acetic acid, the conditions most suitable for their quantitative separation are indicated and discussed.

ПРОТИВОТОЧНЫЙ ИОНОФОРЕЗ—II: ПРАКТИЧЕСКИЕ ПРИМЕНЕНИЯ МЕТОДА:

W. Preetz and H. L. Pfeiffer, *Talanta*, 1967, **14**, 143.

Резюме—С помощью нового прибора удалось подтвердить принципы и течение противоточного ионофореза на основании применения метода на модельные анионные вещества. Качественные исследования показали распределение анионов между анодом и катодом в зависимости от их подвижностей. Для образования стационарного состояния анионы в аноде и противоточных электролитах надо быть более подвижны, а анионы в вытекающем растворе менее подвижны чем анионы в разделяемом растворе. Измерение напряжения поля в камере с капиллярным разделительным зазором показали существование острой перемены напряженности поля на границах стационарных зон; обнаруженные острые разделения получены на основе этого профиля напяжения. На основании сравнения факторов напряжения поля и известных подвижностей удалось вычислить подвижности других ионов. Концентрации ионов в зонах можно вычислить из подвижностей ионов и концентрации противоточного раствора.

КАТИОННЫЙ ОБМЕН НЕКОТОРЫХ ЭЛЕМЕНТОВ В РАСТВОРЕ СОЛЯНОЙ КИСЛОТЫ И ОРГАНИЧЕСКИХ РАСТВОРИТЕЛЕЙ:

J. Korisch and S. S. Ahluwalia, *Talanta*, 1967, **14**, 155.

Резюме—Исследованы катионообменные характеристики 20 элементов на сильнокислой катионообменной смоле Дауекс 50 × 8 в растворах, содержащих различные концентрации органических растворителей и соляной кислоты. Сообщены и обсуждены самые подходящие условия для количественного определения этих элементов, разработанные на основании их коэффициентов распределения в органических растворителях метиловом, этиловом, н-пропиловом и изопроплловом спиртах, метилгликоле, ацетоне, тетрагидрофуране и уксусной кислоте.

Spectrophotometric study of the reaction of the uranyl ion with 4-(2-thiazolylazo)resorcinol: L. SOMMER and V. M. IVANOV, *Talanta*, 1967, **14**, 171 (Department of Analytical Chemistry, J. E. Purkyně University, Brno, Czechoslovakia).

Summary—The uranyl ion forms only 1:1 chelates with 4-(2-thiazolylazo)resorcinol (TAR) in solution, $UO_2(TAR)H^+$ being formed below pH 3 and $UO_2(TAR)$ above pH 3·5. The latter complex may also be precipitated at pH > 3. The quantitative formation of $UO_2(TAR)$ at pH 7·5–7·8 in solutions containing a small excess of reagent and some triethanolamine as buffer can be used for the sensitive spectrophotometric determination of uranium. Several interfering ions can be masked with a mixture of sodium fluoride, cyclohexanediaminetetraacetic acid and 5-sulphosalicyclic acid. TAR is slightly less sensitive than 4-(2-pyridylazo)resorcinol as a reagent for uranium but is more selective.

Determination of alumina film thickness by alpha particle scattering: MAX PEISACH, DARRELL O. POOLE and HERMANN F. RÖHM, *Talanta*, 1967, **14**, 187 (Southern Universities Nuclear Institute, P.O. Box 17, Faure, C.P., South Africa).

Summary—The scattering of accelerated alpha particles has been used to determine the surface oxide film thickness of anodized aluminium. The measurements were based on determining the difference between the energy of an alpha particle scattered from the surface oxide layer and that from the underlying metal. Films ranging in thickness from 10 to 130 $\mu g/cm^2$ were analysed non-destructively with a relative standard deviation of 3·5%. The average time for an analysis was 30 min with an incident beam current of up to about 1 μA.

Analysis of zone-melted ultra-pure organic compounds: A new quantitative differential thermal analysis method: ROBERT FRIEDENBERG and PAUL J. JANNKE, *Talanta*, 1967, **14**, 195 (Department of Neurobiology in Psychiatry, University of Maryland, Baltimore, Maryland, U.S.A.)

Summary—A method for the rapid quantitative determination of impurities in ultra-pure organic compounds is described. It is based on the difference in slopes of the curves obtained when the difference in temperature between the sample and a reference shield is plotted against time. The results are compared with those obtained by thermal analysis.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ИЗУЧЕНИЕ РЕАКЦИИ УРАНИЛИОНА С 4-(2-ТИАЗОЛИЛАЗО)-РЕЗОРЦИНОМ:

L. Sommer and V. M. Ivanov, *Talanta*, 1967, **14**, 171.

Резюме—Уранилион образует только 1:1 хелаты с 4-(2-тиазолилазо)резорцином (TAR) в растворе, $UO_2(TAR)H^+$ образуясь ниже pH 3, а $UO_2(TAR)$ выше pH 3,5. Последный компдекс тоже осаждается при pH выше 3. Количественным образованием $UO_2(TAR)$ при pH 7,5–7,8 в растворах содержащих небольшой избыток реагента и триэтаноламин в качестве буффера можно пользоваться для чувствительного спектрофотометрического определения урана. Некоторые мешающие ионы можно маскировать смесью фторида натрия, циклогександиаминтетрауксусной кислоты и 5-сульфосалициловой кислоты. TAR является незначительно меньше чувствительным чем 4-(2-пиридилазо)резорцин в качестве реагента для урана, но является более избирательным.

ОПРЕДЕЛЕНИЕ ТОЛЩИНЫ ПЛЕНОК АЛЮМИНИЯ МЕТОДОМ РАССЕЯНИЯ АЛЬФА ЧАСТИЦ:

Max Peisach, Darrell O. Poole and Hermann F. Röhm, *Talanta*, 1967, **14**, 187.

Резюме—Рассеяние ускоренных альфа частиц использовано для определения толщины поверхностной пленки окиси анодированного алюминия. Определение основывается на измерении разници между энергией альфа частици рассеяной от поверхностной пленки окиси и альфа частици рассеяной от нижнего слоя металла. Относительная стандартная ошибка при анализе пленок толщины 10–130 мкг/см^2 была 3,5%. Средная продолжительность определения 30 мин. при токе падающего пучка около 1 мкамп.

АНАЛИЗ ОЧИЩЕННЫХ МЕТОДОМ ЗОНАЛЬНОГО ПЛАВЛЕНИЯ ВЫСОКОЧИСТЫХ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ. НОВЫЙ КОЛИЧЕСТВЕННЫЙ МЕТОД ДИФФЕРЕНЦИАЛЬНОГО ТЕРМИЧЕСКОГО АНАЛИЗА:

Robert Friedenberg and Paul J. Jannke, *Talanta*, 1967, **14**, 195.

Резюме—Описан метод для быстрого количественного определения примесей в высокочистых органических соединениях. Метод основывается на разници наклона кривых, представляющих разницу температуры между пробы и эталонного экрана в зависимости от времени. Результаты сравниваются с полученными термическим анализом данными.

Rapid analysis of plating baths by a direct-reading thermometric method: I. SAJÓ and B. SIPOS, *Talanta*, 1967, **14**, 203 (Research Institute for Ferrous Metallurgy, Budapest XI, Fehérvári út 130, Hungary).

Summary—Methods are described for the rapid analysis of plating baths by measurement of the heat evolved in a reaction between the reagent and the component to be determined. The novel feature of the method is the use of reagents which have zero heat of mixing, so that the temperature scale can be directly calibrated in concentration units for a particular determination. A determination takes only 5 min and the precision is equal to that of the classical methods. Procedures are given for the analysis of nickel and chromium plating baths.

Improved method for the constant-current potentiometric determination of plutonium: CHARLES E. PIETRI and ALBERT W. WENZEL, *Talanta*, 1967, **14**, 215 (U.S. Atomic Energy Commission, New Brunswick, N.J., U.S.A.)

Summary—A highly precise method is described for the determination of plutonium by constant-current potentiometric titration with primary standard potassium dichromate. The relative standard deviation is 0·04% or better.

An experimental evaluation of neutron activation, wet assay and fire assay methods of determining gold in ores: A. CHOW and F. E. BEAMISH, *Talanta*, 1967, **14**, 219 (Department of Chemistry, University of Toronto, Toronto 5, Canada).

Summary—The errors associated with fire assay, wet extraction and neutron activation methods are evaluated, the accuracy and precision of these methods are compared, and a method for determining the chemical recovery in the activation determination of gold in ores and concentrates is presented.

БЫСТРЫЙ АНАЛИЗ ГАЛЬВАНИЧЕСКИХ РАСТВОРОВ С ИСПОЛЬЗОВАНИЕМ ТЕРМОМЕТРИЧЕСКОГО МЕТОДА С ПРЯМЫМ ОТСЧЁТОМ:

I. Sajó and B. Sipos, *Talanta*, 1967, **14**, 203.

Резюме—Описаны методы для быстрого анализа гальванических растворов измерением теплоты, выделеной реакцией между реагентом и определяемым компонентом. Новое в этом методе использование реагентов имеющих теплоту смешения нуль, так что дана возможность директной калибровки температурной шкалы в единицах концентрации для определенного анализа. Одно определение требует только 5 минут, а точность метода равна точности классических методов. Приведены процедуры для анализа гальванических растворов никеля и хрома.

УЛУЧШЕННЫЙ МЕТОД ПОТЕНЦИОМЕТРИЧЕСКОГО ОПРЕДЕЛЕНИЯ ПЛУТОНИЯ ПРИ ПОСТОЯННОМ ТОКЕ:

Charles E. Pietri and Albert W. Wenzel, *Talanta*, 1967, **14**, 215.

Резюме—Описывается весьма аккуратный метод определения плутония основывающийся на потенциометрическом титровании стандартным раствором бихромата калия при постоянном токе. Относительная стандартная ошибка лучше чем 0,04%.

ОЦЕНКА МЕТОДОВ НЕЙТРОННОЙ АКТИВАЦИИ, МОКРОЙ ПРОБЫ И СУХОЙ ПРОБЫ ДЛЯ ОПРЕДЕЛЕНИЯ ЗОЛОТА В РУДАХ:

A. Chow and F. E. Beamish, *Talanta*, 1967, **14**, 219.

Резюме—Рассмотрены ошибки при определении золота сухим путем, экстрагированием и нейтроноактивационным методом. Сравнивается точность и воспроизводимость этих методов и предложен метод определения химического выхода при активационном определении золота в рудах.

Use of thenoyltrifluoroacetone for the determination of manganese by activation analysis: FRANTIŠEK KUKULA, BLAŽENA MUDROVÁ and MILOSLAV KŘIVÁNEK, *Talanta*, 1967, **14**, 233 (The Nuclear Research Institute, Czechoslovak Academy of Sciences, Řež by Prague, Czechoslovakia).

Summary—A new procedure for the substoichiometric extraction of bivalent manganese by thenoyltrifluoroacetone into ethyl acetate has been developed and used in activation analysis. The value of the extraction constant has been found to be $3{\cdot}1 \times 10^{-6}$; the pH range in which the extraction can be performed is 7·8–9·2. The influence of oxalate, citrate, tartrate, fluoride and cyanide ions has been studied. A selective substoichiometric extraction of manganese in the presence of Zr, Hf, Nb, Th, Fe and Sc is possible at pH 8–8·5, tartrate and fluoride being used as masking agents. Copper and cobalt can be screened by ammonia and cyanide respectively. The method has been used for the determination of manganese in biological materials, potassium fluoride and zirconium.

Inorganic polarography in organic solvents—II: Polarographic examination of the molybdenum(V) thiocyanate complex in diethyl ether: B. K. AFGHAN and R. M. DAGNALL, *Talanta*, 1967, **14**, 239 (Chemistry Department, Imperial College, London, S.W.7, England).

Summary—A procedure involving the solvent extraction of molybdenum(V) thiocyanate into diethyl ether followed by a direct polarographic examination of the organic phase offers a selective method for the determination of molybdenum down to 0·5 ppm. Only molybdenum, amongst 21 elements examined, is observed to give a reduction wave under the recommended conditions. The method is evaluated with respect to various experimental factors and is applied to the determination of molybdenum in mild and alloy steels.

Determination of low concentrations of hydrogen halides and halogens in the gas phase. Removal from a mixture of gases and quantitative estimation: LESLIE BATT and FRANK R. CRUICKSHANK, *Talanta*, 1967, **14**, 245 (Chemistry Department, University of Aberdeen, Old Aberdeen, Scotland).

Summary—A method has been developed for the removal of hydrogen chloride, and mixtures of bromine and hydrogen bromide, from gaseous mixtures by absorption on various solids. The efficiency of removal of bromine and hydrogen bromide has been determined and the substances have been estimated potentiometrically. The technique is extended to include the other halogens and hydrogen halides.

ИСПОЛЬЗОВАНИЕ ТЕНОИЛТРИФТОРАЦЕТОНА ДЛЯ ОПРЕДЕЛЕНИЯ МАРГАНЦА МЕТОДОМ АКТИВАЦИОННОГО АНАЛИЗА:

FRANTISEK KUKULA, BLAZENA MUDROVA and MILOSLAV KRIVANEK, *Talanta*, 1967, **14**, 233.

Резюме—Разработана и применена в активационном анализе новая процедура для извлечения двувалентного марганца теноилтрифторацетоном в растворе этилацетата. Константа экстракции равна $3{,}1 \times 10^{-6}$; извлечение проводится в области pH 7,9–9,2. Изучено влияние ионов оксалата, цитрата, тартрата, фторида и цианида. Можно провести селективное субстехиометрическое извлечение марганца в присутствии Zr, Hf, Nb, Th, Fe, и Sc при pH 8–8,5, с использованием тартрат—и фторидионов в качестве маскирующих агентов. Медь и кобальт можно маскировать аммиаком или цианидионом, соответственно. Методом пользовались для определения марганца в биологических веществах, в фториде калия и цирконии.

ИЕОРГАНИЧЕСКАЯ ПОЛЯРОГРАФИЯ В ОРГАНИЧЕСКИХ РАСТВОРИТЕЛЯХ—II. ПОЛЯРОГРАФИЧЕСКОЕ ИЗУЧЕНИЕ КОМПЛЕКСА ТИОЦИАНАТА МОЛИБДЕНА(V) В ЭТИЛОВОМ ЭФИРЕ:

B. K. AFGHAN and R. M. DAGNALL, *Talanta*, 1967, **14**, 239.

Резюме—Описывается избирательный метод определения молибдена все до 0,5 мг/л основывающийся на экстрагировании тиоцианата молибдена(V) этиловым эфиром и прямом исследовании органической фазы полярографическим методом. Среди 21 исследованных элементов только молибден дает волну восстановления в предложенных условиях. Исследованы различные экспериментальные факторы влияющие на метод, а методом пользовались для определения молибдена в мягких и легированных сталях.

ОПРЕДЕЛЕНИЕ НЕБОЛЬШИХ КОНЦЕНТРАЦИЙ ГАЛОИДОВОДОРОДОВ И ГАЛОИДОВ В ГАЗОВОЙ ФАЗЕ. УДАЛЕНИЕ ИЗ СМЕСИ ГАЗОВ И КОЛИЧЕСТВЕННОЕ ОПРЕДЕЛЕНИЕ:

LESLIE BATT and FRANK R. CRUICKSHANK, *Talanta*, 1967, **14**, 245.

Резюме—Разработан метод удаления хлороводорода и смесей брома и бромоводорода из смесей газов адсорбированием на различных твердых фазах. Определена эффективность удаления брома и бромоводорода и проведена оценка их концентраций потенциометрическим методом. Методом можно пользоваться и для определения других галоидов и галоидоводородов.

Polarography of lead itaconate complexes: TSAI-TEH LAI, SHOU-NAN CHEN and EYIH LIN, *Talanta*, 1967, **14**, 251 (Analytical Chemistry Laboratory, Cheng Kung University, Tainan, Taiwan, China).

Summary—The complexation of lead ions with itaconic acid (H_2A) has been studied polarographically at 30°. At $pH < pK_1$, the complex species $Pb(HA)^+$ was identified. At $pK_1 < pH < pK_2$ and $pH > pK_2$ the formation of Pb(A) and $Pb(A)_3^{4-}$ respectively, was confirmed. The dissociation constant of $Pb(A)_2^{2-}$ was found to be $8{\cdot}3 \times 10^{-6}$. The electrode reactions were established.

Free radical oxidation of dihydric phenols with diphenylpicrylhydrazyl: GEORGE H. SCHENK and DANIEL J. BROWN, *Talanta*, 1967, **14**, 257 (Department of Chemistry, Wayne State University, Detroit 2, Michigan, U.S.A.)

Summary—A spectrophotometric study has been made of the reactions between the free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) and the three dihydric phenols. It has been shown that water affects the rate of all three reactions and the stoichiometry of the DPPH-catechol (pyrocatechol) reaction. Because of the differences in the rate of oxidation in absolute ethanol, it is possible to determine selectively either hydroquinone or catechol in the presence of resorcinol.

Precise determination of uranium in pure uranium and uranium compounds by constant-current coulometric titration: JERZY MALINOWSKI, *Talanta*, 1967, **14**, 263 (International Atomic Energy Agency, Seibersdorf Laboratory, Seibersdorf, Niederösterreich, Austria).

Summary—A procedure is described for very precise determination of uranium in high-purity uranium and uranium compounds. Uranium(VI) is reduced in a concentrated hydrochloric acid solution by metallic aluminium in the presence of cadmium ions to uranium(III). This is oxidized to uranium(IV) by protons on addition of an excess of orthophosphoric acid, and then oxidized to uranium(VI) by adding a weighed quantity of potassium dichromate in small excess. The excess of potassium dichromate is determined by constant-current coulometry. The coefficient of variation does not exceed 0·003%.

Contributions to the basic problems of complexometry—XXII: Determination of thorium and scandium in the presence of each other: R. PŘIBIL, V. VESELÝ and J. HORÁČEK, *Talanta*, 1967, **14**, 266 (Analytical Laboratory, J. Heyrovský Polarographic Institute, ČSAV, Prague 1, Jilská 16, Czechoslovakia).

Summary—A new method for the determination of thorium and scandium in the presence of each other is presented. Two aliquots of the solution are necessary. In one the sum of thorium and scandium is determined by direct titration with DCTA. In the second, thorium and scandium are treated with an excess of TTHA, phosphate is added, and zinc is used to titrate the excess of TTHA and to displace the scandium from its TTHA complex.

ПОЛЯРОГРАФИЯ КОМПЛЕКСОВ СВИНЦА И ИТАКОНОВОЙ КИСЛОТЫ:

TSAI-TEH LAI, SHOU-NAN CHEN and EYIH LIN, *Talanta*, 1967, **14**, 251.

Резюме—Образование комплексов между ионами свинца и итаконовой кислоты (H_2A) изучено полярографическим методом при 30°. При $pH < pK_1$ обнаружен комплекс $Pb(HA)^+$. При $pK_1 < pH < pK_2$ и $pH > pK_2$ подтверждено образование комплексов $Pb(A)$ и $Pb(A)_2^{2-}$. Константа диссоциации комплекса $Pb(A)_2^{2-}$ равна $8{,}3 \times 10^{-5}$. Определены электродные реакции.

ОКИСЛЕНИЕ ПУТЕМ СВОБОДНЫХ РАДИКАЛОВ ДВУАТОМНЫХ ФЕНОЛОВ С ИСПОЛЬЗОВАНИЕМ ДИФЕНИЛПИКРИЛГИДРАЗИЛА:

GEORGE H. SCHENK and DANIEL J. BROWN, *Talanta*, 1967, **14**, 257.

Резюме—Изучены спектрофотометрическим методом реакции свободного радикала 2,2-дифенил-1-пикрилгидразила(ДФПГ) и трех двуатомных фенолов. Показано что вода влияет на скорость этих трех реакций и на реакцию ДФПГ с катехином (пирокатехином). На основании различных скоростей окисления в абсолютном спирте удается избирательно определять гидрохинон или катехин в присутствии резорцина.

АККУРАТНОЕ ОПРЕДЕЛЕНИЕ УРАНА В ЧИСТОМ УРАНЕ И В СОЕДИНЕНИЯХ УРАНА МЕТОДОМ КУЛОНОМЕТРИЧЕСКОГО ТИТРОВАНИЯ ПРИ ПОСТОЯННОМ ТОКЕ:

JERZY MALINOWSKI, *Talanta*, 1967, **14**, 263.

Резюме—Предложена процедура весьма аккуратного определения урана в высокочистом уране и в урановых соединениях. Уран(VI) восстанавливаю до урана(III) металлическим алюминием в растворе концентрированной соляной кислоты в присутствии ионов кадмия. Уран(III) окисляют до урана(IV) протонами добавлением избытка ортофосфорной кислоты, а затем окисляют до урана(VI) добавлением взвешенного количества бихромата калия в небольшем избытке. Этот избыток бихромата калия определяют кулонометрическим титрованием при константном токе. Коэффициент вариации не превосходит 0,003%.

ВКЛАД К ОСНОВНЫМ ПРОБЛЕМАМ КОМПЛЕКСОМЕТРИИ—XXIII: ОПРЕДЕЛЕНИЕ ТОРИЯ И СКАНДИЯ ОДНОГО В ПРИСУТСТВИИ ДРУГОТО:

R. PŘIBIL, V. VESELÝ and J. HORÁČEK, *Talanta*, 1967, **14**, 266.

Резюме—Сообщен новый метод определения тория и скандия одного в присутствии другого. Требуются две аликвотных части раствора. В одной части определяют сумму тория и скандия прямым титрованием с ДЦТА. Во второй части раствору добавляют избыток ТТХА и фосфатионы а затем оттитровывают избыток ТТХА и вытесняют скандий из его комплекса с ТТХА с раствором цинка.